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ADSORPTION AND DIFFUSION OF OXYGEN, NITROGEN, METHANE AND ARGON IN MOLECULAR SIEVE CARBONS

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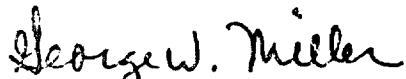
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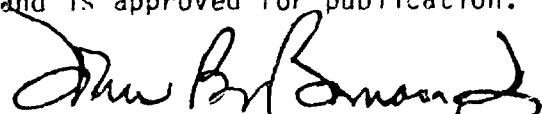
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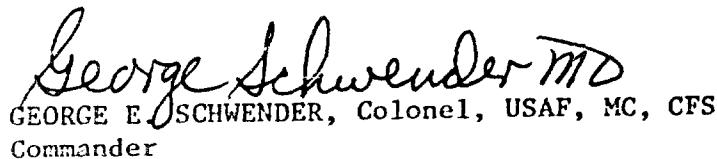
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Equilibrium adsorption and diffusion data for oxygen, nitrogen, methane and argon in carbon molecular sieves 3A and 5A at 0°C, 30°C and 50°C were obtained at pressures up to 13 Bar using a high-pressure Cahn electrobalance. On a molar basis, methane had the highest adsorption capacity among the four gases studied both in 3A and 5A molecular sieve carbons. Oxygen and nitrogen had approximately the same equilibrium adsorption capacity. Equilibrium adsorption data were represented by a Langmuir equation and the Vacancy Solution Model (VSM). The VSM appears to give a good fit of the experimental data while the representation of the experimental data by the Langmuir equation showed deviation, especially at high pressures. The isosteric heats of adsorption were found to increase slightly with an increase in surface coverage. The values were slightly higher on 3A than on 5A for all the gases except argon. Kinetic data showed that oxygen has the highest diffusion rate and methane the lowest. Diffusivities increased with temperature. At low temperature the diffusivity for nitrogen increased with pressure. No pressure dependency was observed for the diffusivity of the other gases.

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SUMMARY

An important development in adsorption technology is pressure swing adsorption (PSA) in which periodical regeneration of the adsorbent is accomplished by reducing total pressure. Large throughputs can generally be obtained from a small-scale PSA adsorber by using a short cycle time (in minutes or seconds) which results in rapid pressure cycling. Small-scale PSA adsorbers are presently used to produce breathable oxygen on board military aircraft. The mechanisms for separation in PSA are mainly based on kinetic or equilibrium effects although the use of the steric effect is also possible (e.g. molecular sieve). Consequently, understanding both equilibrium and kinetic data is essential in designing a better PSA process. This report describes the technical efforts to compile the equilibrium and kinetic data of several gases in molecular sieve carbons (MSC) with the objective that the results can be applied to the design of a PSA process for air separation.

Equilibrium adsorption and diffusion of oxygen, nitrogen, methane and argon in carbon molecular sieves 3A and 5A were investigated. Equilibrium as well as kinetic data were compiled during the adsorption experiments in two different gravimetric setups, one for high pressures and the other for low pressures, although most runs were made in the high pressure unit. The experimental data are tabulated in the Appendix. The adsorbate pressure was varied over a wide range, viz., 0-10,000 Torr at three temperatures, 0°C, 30°C and 50°C. Both high pressure and low pressure adsorption experiments were carried out gravimetrically.

On a molar basis, methane had the highest adsorption capacity among the four gases studied in both 3A and 5A molecular sieve carbons. Oxygen and nitrogen had approximately the same equilibrium adsorption capacity. Equilibrium adsorption data are represented by a Langmuir equation and the vacancy solution model (VSM). The VSM model appears to give a good fit to the experimental data. Experimental evidences also showed that MSC adsorbed relatively small amounts of water when it was exposed to ambient air for an extended period. This hydrophobic property of MSC makes it especially suitable for air separation in a pressure swing operation.

The isosteric heats of adsorption were found to increase slightly with increases in the surface coverage. The values are slightly higher on 3A than on 5A for all the gases except argon, indicating that 3A MSC showed a greater energetic heterogeneity than 5A MSC although both MSCs showed a relatively low energetic heterogeneity.

Kinetic data showed that oxygen had the highest diffusion rate while methane had the lowest rate. Methane adsorption in 3A was considerably slower than in 5A MSC. The adsorption of oxygen

in both 5A and 3A occurred at about the same rate. Nitrogen and argon adsorption in 3A was slower than in 5A. The diffusivity values obtained from the kinetic data showed no dependency on pressure but increased with increasing temperature as expected.

The high adsorption rate of oxygen in both 3A and 5A MSC coupled with the fact that both argon and nitrogen had a slower adsorption rate in 3A than in 5A implies that 3A may be a better adsorbent for kinetic separation of air components in a pressure swing operation.

Recommendations are made for a follow-up program to employ the newly designed multicomponent adsorption setup to collect data for the adsorption and diffusion of binary gases at 0°C, 30°C, and 50°C in a pressure range of 0-10,000 Torr. Both the effects of co-adsorption of binary gases and the displacement phenomena should be investigated. Furthermore, it is also recommended to continue the investigation of model prediction for multicomponent adsorption from single component adsorption data. The Langmuir, VSM, IAST and modified Langmuir-Sips isotherm equations should be used to predict multicomponent adsorption isotherms from single component data. The mixture adsorption isotherms developed from the model should be compared with those developed from experimental measurements. Furthermore, the development of a mathematical model for multicomponent diffusion is recommended.

ADSORPTION AND DIFFUSION OF OXYGEN, NITROGEN, METHANE AND ARGON IN MOLECULAR SIEVE CARBONS

I. INTRODUCTION

It is well known that coals and their carbonized product show molecular sieve properties although their adsorption capacities are generally too low to have any practical use. There is, however, considerable information in the literature about the production of carbons with both molecular sieve properties and high adsorption capacity from carbonization of organic polymers (1-3). Carbons with molecular sieving properties were first observed by Franklin (4) who reported that heat treated coals excluded fluids according to their molecular sizes. Dacey and Thomas (5) later reported an extensive study on the properties of a hard, highly porous charcoal prepared by the pyrolysis of polyvinylidene chloride. Their results clearly showed the molecular sieving properties of the charcoal. Extensive reviews on the subject have been reported by Walker et al (6) and Spencer and Bond (7). As an adsorbent, carbon molecular sieves may be preferred to inorganic molecular sieves due not only to their stability at higher temperatures and in acidic media but also due to their lower affinity to water (6). Furthermore, from a practical point of view, molecular sieve carbons are attractive because they can be easily obtained by pyrolysis of many thermosetting polymers such as poly (vinylidene chloride) (PVDC) (5, 8), poly (furfuryl alcohol) (9), cellulose (10), cellulose triacetate (11), saran copolymer (12), poly (di vinylbenzene) (13), and various coals such as anthracite (14) and the bamboo (15). Thus, the fact that the effective pore size can be adjusted by the conditions of the manufacturing process makes it relatively easy to tailor a carbon sieve for a specific separation. However, the difficulty involved in achieving absolute reproducibility between different batches (16) and the existence of a distribution of pore size, even if narrow, make the molecular sieving selectivity of a carbon sieve not as good as that of a zeolite sieve. Nevertheless, the remarkably high kinetic selectivity which may be attained with a well-prepared carbon sieve coupled with its low water affinity makes carbon sieve a prime adsorbent for air separation.

A number of current and proposed applications of carbon sieves has been reviewed by Jüntgen (17). It should be pointed out that currently the most important large-scale application for carbon sieve is in air separation. It should further be pointed out that its deterioration due to oxidation does not appear to be a significant problem. Other potential applications include the clean-up of the off-gases from nuclear facilities and the production of pure hydrogen from gas streams containing small

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amounts of hydrocarbons. However, a wider range of process applications will emerge as the technology of producing carbon sieves is further developed.

The present study reports an investigation of the adsorption and diffusion of nitrogen (N_2), oxygen (O_2), methane (CH_4) and argon (Ar) in 5A and 3A molecular sieve carbons. The prime objective was to investigate the effects of molecular size on the equilibrium adsorption and diffusion property of these molecular sieve carbons. It is anticipated that the results obtained in the present study can be applied to the design of a pressure swing adsorption (PSA) process for air separation.

II. EXPERIMENTAL

The adsorption of pure gases by 5A and 3A MSC (20-40 mesh) was studied at 0°, 30°, and 50°C. The adsorbate pressure was varied over a wide range, *viz.*, 0-10,000 Torr. Equilibrium as well as kinetic data were compiled during the adsorption experiments in two different gravimetric setups, one for high pressures and the other for low pressures although most runs were made in the high pressure unit.

The high-pressure adsorption experiments were carried out in a gravimetric setup constructed using mainly 316 stainless steel. A Cahn 1000 electrobalance was placed inside a stainless steel casing; it was connected to a gas reservoir, gas supply tank and a pumping system using thick-walled stainless steel tubing and precision Nupro valves. Pressures up to 50 Bars could be safely reached in the setup shown schematically in Figure 1. Photographs of the high pressure unit are shown in Figure 2.

The entire system could be evacuated to a pressure less than 10^{-3} Torr by means of an oil-free turbo pump (Varian V80A) in conjunction with a mechanical roughing pump. The weight change during experiments could be determined with an accuracy of 0.5 micrograms. The weight, temperature, and pressure could be monitored continuously with an AT&T personal computer. The pressure was measured using MKS Baratron gauges. Omega digital controllers were used for temperature control and measurement.

Additional experiments in the subatmospheric pressure range (0-760 Torr) were also carried out in an all-glass unit housed in an insulated box free from any kind of disturbance, either mechanical or thermal. The apparatus is shown schematically in Figure 3. Photographs of the unit are shown in Figure 4. The setup consisted of a Cahn 2000 electrobalance mounted inside a glass chamber that could be evacuated to a pressure less than 10^{-4} Torr by means of an oil-free turbo pump (Varian V80A) in conjunction with a mechanical roughing pump. The change in the weight of the sample during experiments could be determined with an accuracy of 0.5 micrograms. The weight, temperature, and

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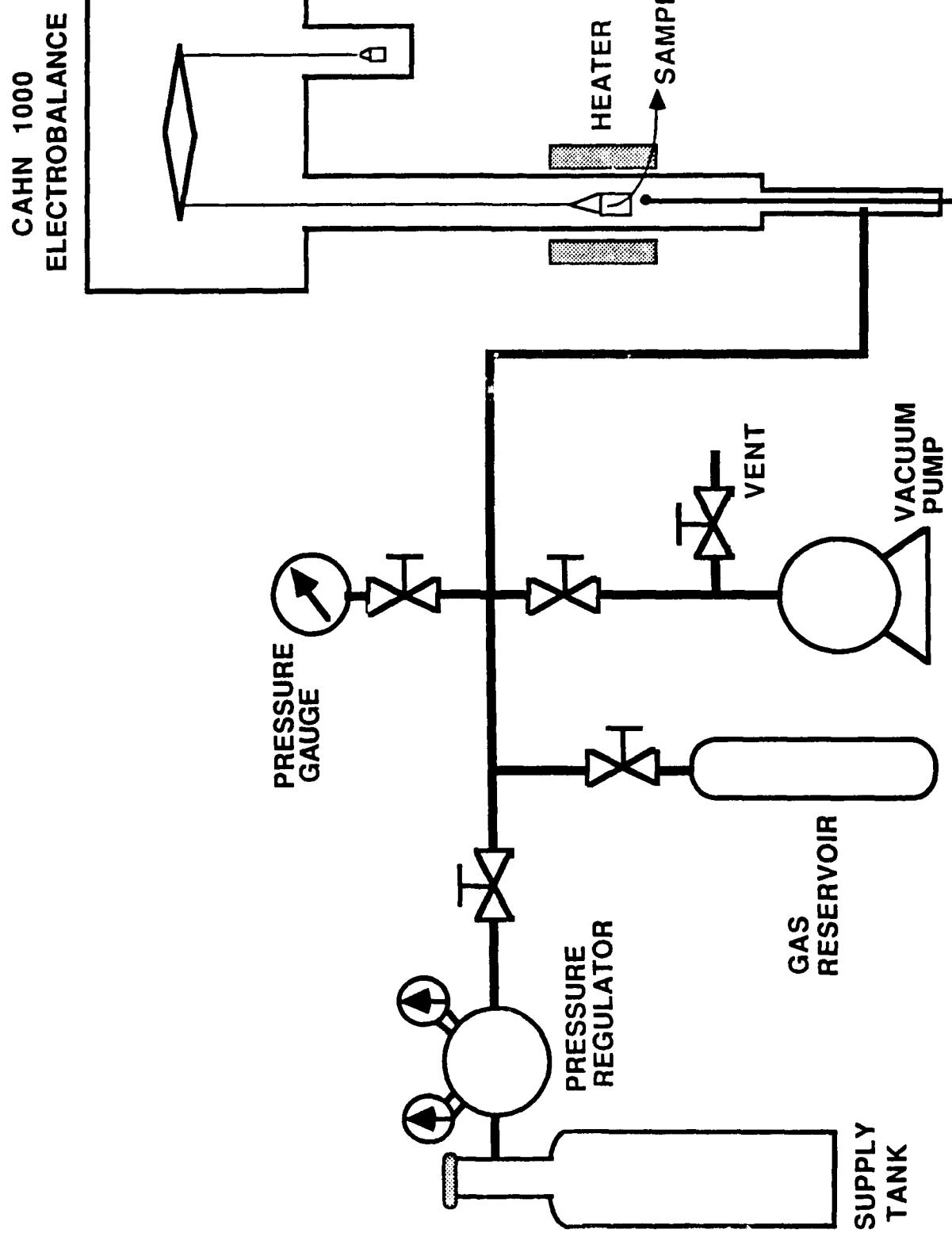
Figure 1. High pressure (0-10,000 Torr) adsorption unit.
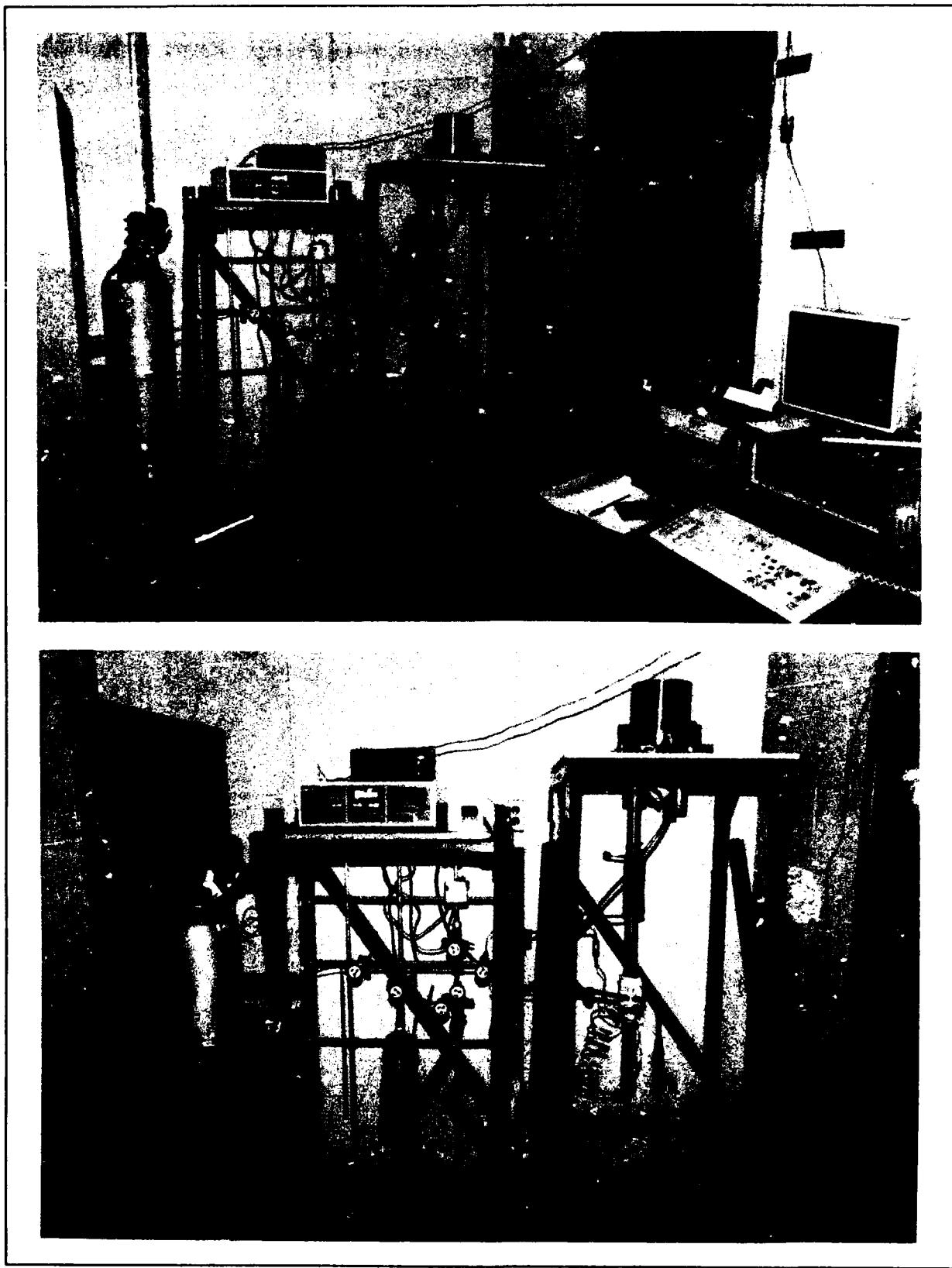
Figure 2.   Photographs of the high pressure adsorption unit.

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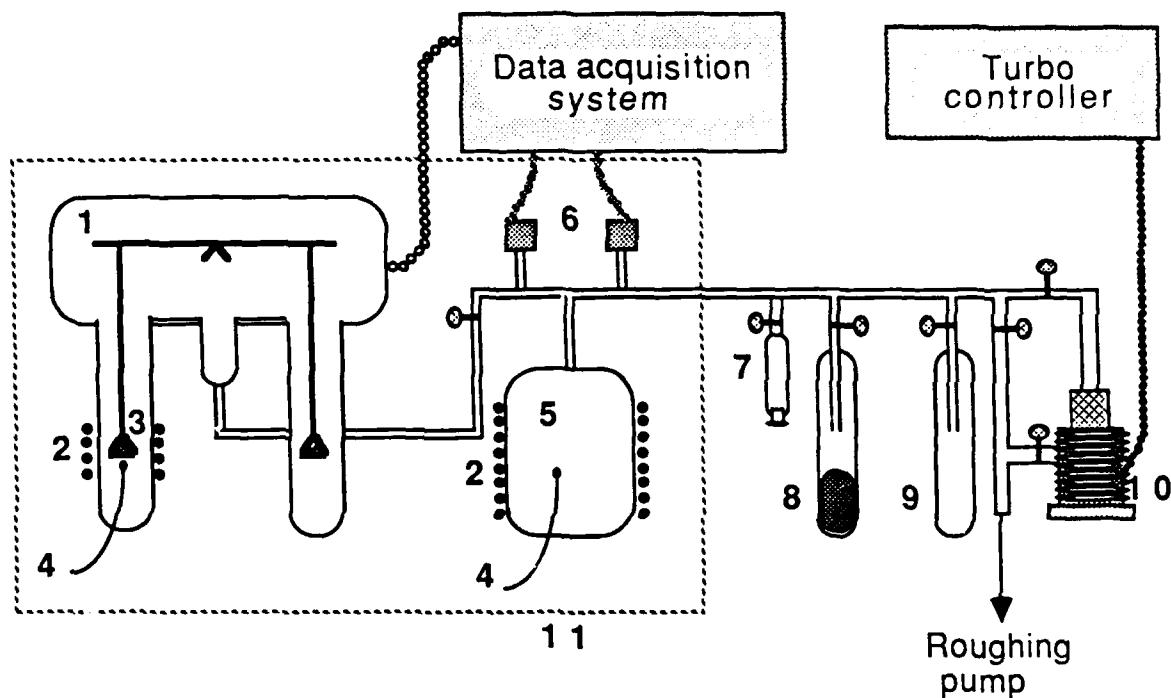
1. Balance assembly
2. Controlled heaters
3. Sample
4. Thermocouples
5. Gas reservoir

6. Pressure sensors
7. Injection assembly
8. Zeolite trap
9. Cold trap
10. Turbomolecular pump

11. Insulated box

Figure 3. Schematic of the low-pressure (0 - 760 Torr) adsorption system.
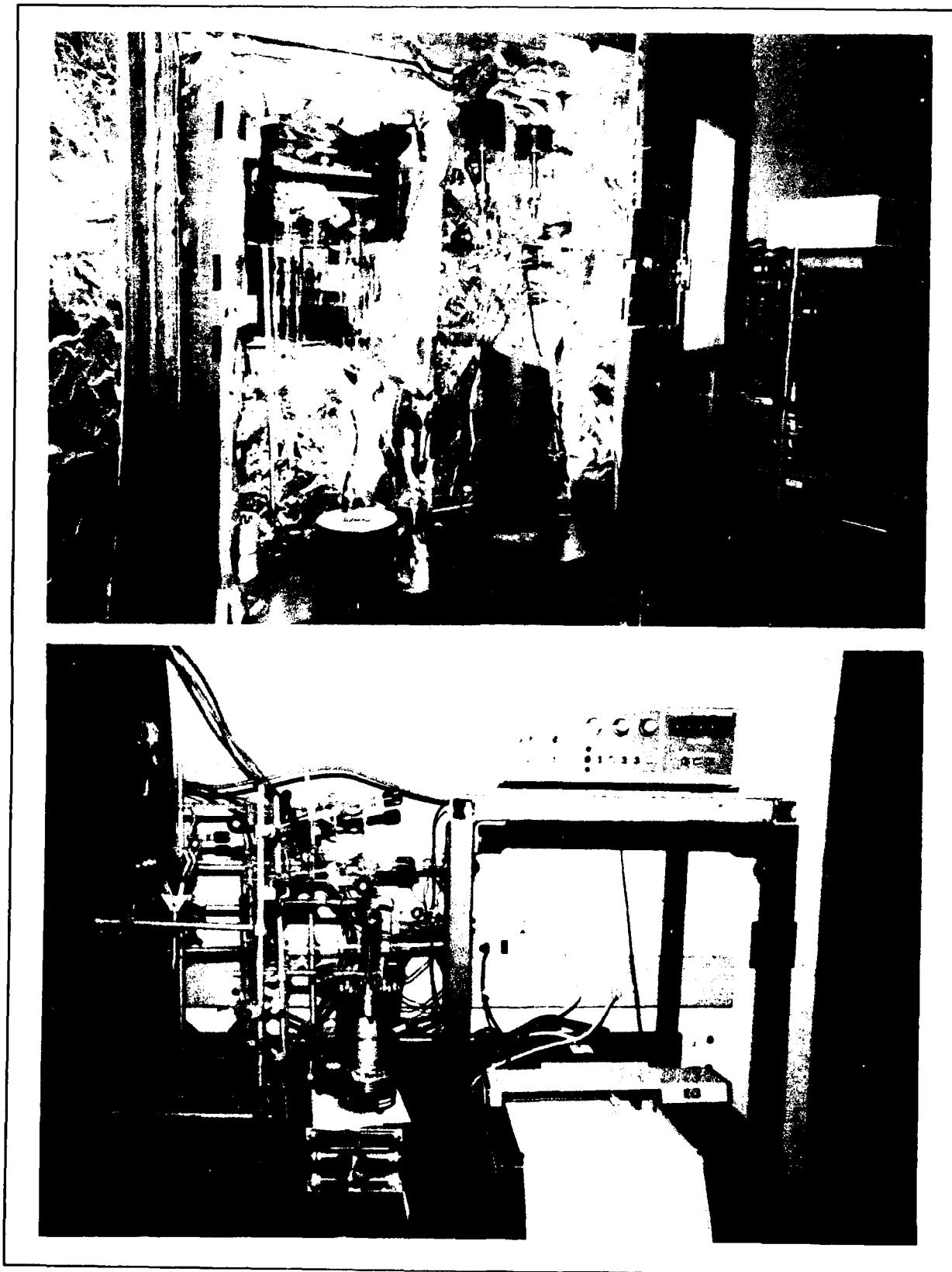
Figure 4. Photographs of the low pressure adsorption unit.

pressure could be monitored continuously using a three-channel chart recorder. The pressure was measured using MKS Baratron gauges. Omega 4002 digital controllers were used for temperature control and measurement.

The sample was activated at 300°C under vacuum for an extended period (6 h). After activation, the sample was allowed to cool to the desired temperature. The gas in the gas reservoir was then expanded into the adsorption system and the weight increase of the sample was continuously recorded. After equilibrium was reached, additional gas was admitted to the adsorption system for a second equilibrium adsorption measurement. The process was repeated until the system reached its final pressure (760 Torr for the subatmospheric unit and approximately 5,000-10,000 Torr for the high pressure unit). Multiple runs were made to assure the reproducibility of the data, which were generally very good as shown in the figures.

The experimental data are given in Appendix A. Each data set contains brief information regarding the experimental conditions. Adsorption isotherms presented in figures were obtained from the pressure vs. equilibrium adsorption amounts tabulated in Appendix A with a reference to the corresponding figure. Uptake rate data giving adsorbed amounts vs. time are also given in Appendix A.

The 3A and 5A molecular sieve carbons (MSC) were manufactured by Takeda Chemical Industries, LTD of Tokyo, Japan, and provided by TIGG Corporation of Pittsburgh, PA. Some of the pertinent information on the MSC samples are summarized in Table 1. The scanning electron micrographs of both 3A and 5A MSC are shown in Figure 5.

TABLE 1. PROPERTIES OF THE MSC SAMPLES

Particle size: 20 - 40 mesh
Bulk density: 0.59 g/cm^3
Sample weight: ˜ 80 mg
Activation temperature: 300°C under vacuum
Duration of activation: 6 hours

III. RESULTS AND DISCUSSION

Activation Procedure

To examine the effect of activation on the initial sample weight loss, about 86 mg of sample (5A MSC, 20-40 mesh) was placed in the electrobalance of the low-pressure unit; its weight-loss was monitored as evacuation proceeded at room
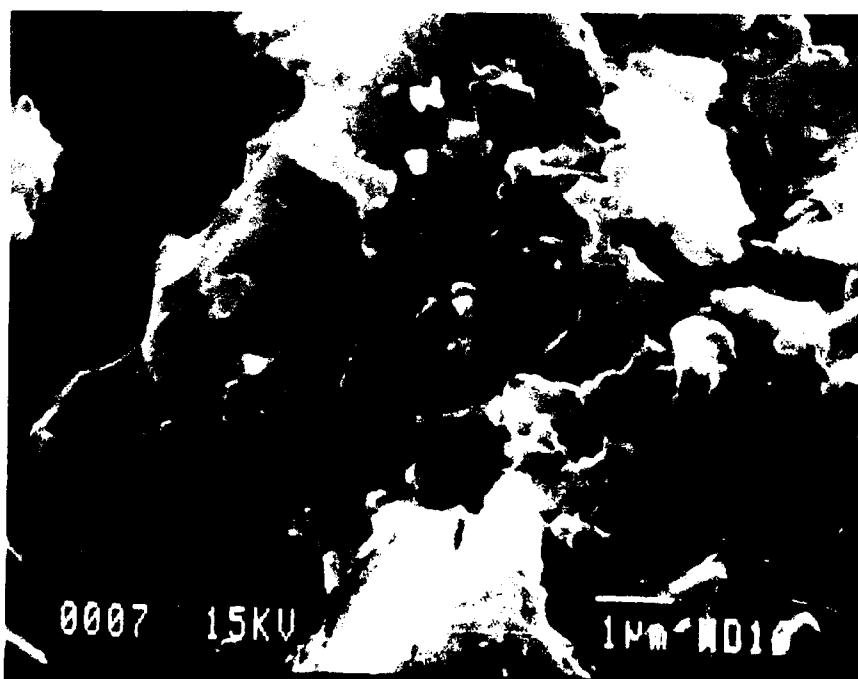
Figure 5.   Scanning electron micrographs of molecular
            sieve carbon 5A (top) and 3A (bottom).

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temperature. Figure 6 shows the weight measurements (expressed as a percentage of initial weight) obtained at various stages during the pump-down. The weight-loss was, roughly speaking, linearly proportional to the pressure decrease from the initial one atmosphere. Calculations showed that if Henry's law ($w = K'P$, where P is the pressure in Torr, w is the adsorbed amount in mg/g and K' is a constant in mg/g·Torr), as applied to adsorption, were employed to model the equilibrium desorption data for 5A MSC in Figure 6, the constant K' was equal to 58.9 (mg/g of adsorbed weight per Torr). This value was close to that obtained later for the adsorption of N_2 or O_2 (K'= 66.2), indicating that the sample mostly adsorbed air while it was under room conditions. Total weight loss during desorption at room temperature was about 1.5% (= 15 mg/g). After a pressure below 10^{-4} Torr was reached in the system, the sample was activated at 100°C, 200°C, and 300°C, successively, each time for 6 hours. After cooling the sample down to room temperature it was observed that there was virtually no additional weight loss during these activation (heating) steps. Figure 6 also shows the weight loss during pump down for 3A MSC. A total loss of only 0.9% by this sample clearly indicates that 3A adsorbed even less amounts of gases and vapors than 5A MSC while it was stored under room conditions. Our observation that the MSC adsorbs negligible amounts of moisture is consistent with the hydrophobic property generally observed in MSC.
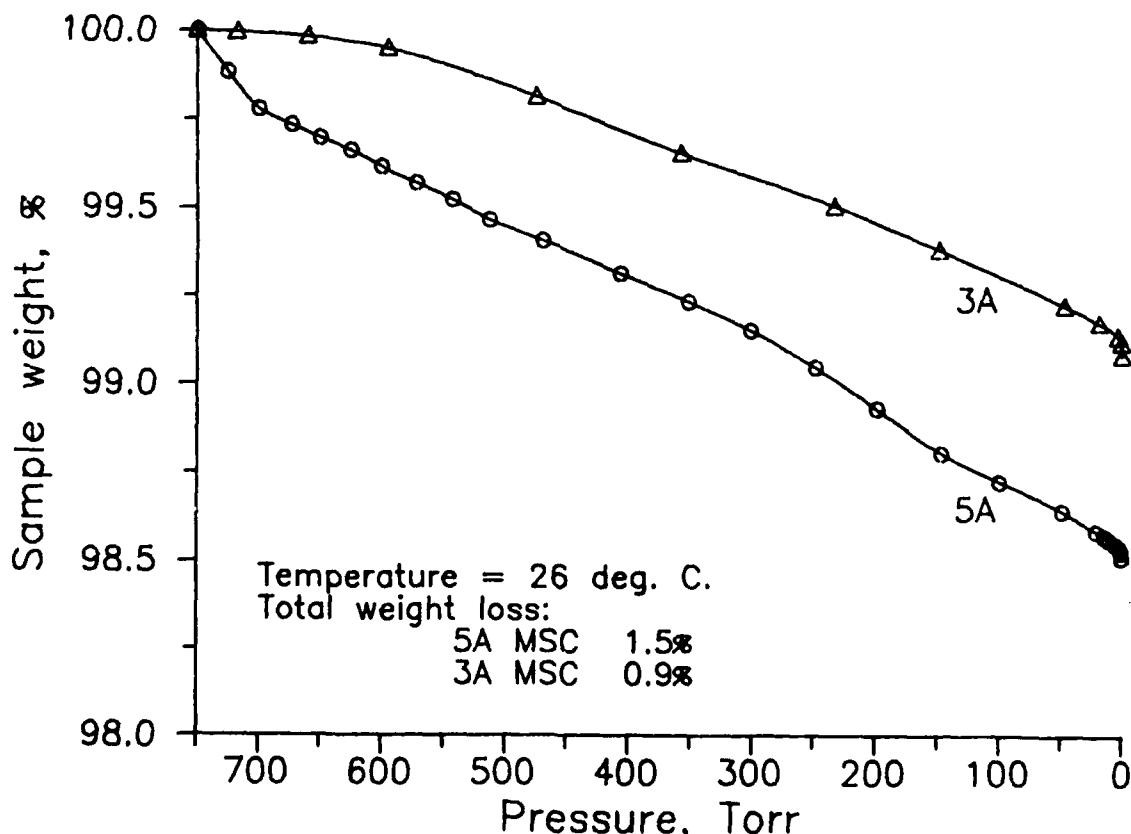
Figure 6. Weight change during initial pump-down.

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Experimental evidence from the low pressure unit appears to show that it is unnecessary to activate the sample at high temperature; however, unless stated otherwise, the runs reported here were performed after the samples were activated at a higher temperature (300°C) for 6 hours to ensure uniform sample pretreatment in both the high pressure and low pressure units. It was not possible to completely regenerate the sample without heating after the sample had been exposed to high pressure gases.

Single Component Adsorption

Model Differentiation

The Langmuir Isotherm   The Langmuir isotherm exhibits Type I (Brunauer, Deming, Deming and Teller (BDDT) classification) behavior which is generally characterized by a long flat branch normally horizontal. The mathematical representation of the Langmuir isotherm is shown in Eq. (1):

$$\frac{q}{q_m} = \frac{b\,P}{1 + b\,P} \tag{1}$$

where q is the adsorption capacity, P is the pressure, q_m is the monolayer coverage, and b is a constant. In this work, the constants q_m and b were determined from experimental adsorption isotherm data by plotting $1/q$ against $1/P$. Equation (1) suggests that such a plot gives a straight line with a slope equal to $1/(q_m b)$ and a y-axis intercept equal to $1/q_m$.

Type I isotherms are frequently encountered with adsorbents such as charcoal and zeolite 13X. The classical interpretation of Type I isotherms is based on the assumptions that the adsorbed layer on the pore wall is only one molecule thick and that the completion of this monolayer gives the plateau of the isotherm. This mechanism was first developed by Langmuir for application to adsorption on an open surface which is freely exposed to the gas phase. The extension of the Langmuir isotherm to microporous adsorbents represents a rather long extrapolation, especially as the channels may be many hundreds or even thousands of molecular diameters in length. Further deviations from the simple Langmuir model can arise from the overlapping of the potential field and from irregularities in the channel producing variations in the extent of overlapping from place to place along the pores. Thus, the assumption of a uniform potential over the entire surface is rarely valid. Nevertheless, the Langmuir isotherm is frequently used to describe an adsorption isotherm exhibiting Type I behavior. One may, thus, regard this as an empirical two-parameter fit of a curve rather than attaching theoretical significance to the fit in the context of the development originally proposed by Langmuir.

The Vacancy Solution Model Suwanayuen and Danner (18) developed a gas adsorption isotherm equation based on vacancy solution theory. The model was later improved by Cochran et al (19, 20). The vacancy solution model (VSM) assumes the existence of a hypothetical solvent called "vacancy" to be filled by adsorbate molecules. Phase equilibrium between the gas and the adsorbed solutions is assumed to exist and excess properties in relation to a dividing surface are used to define the properties of the adsorbed phase. Using the chemical potential expression derived by Lucassen-Reynders (21-23), Danner and his co-workers formulated the following isotherm equation:

$$P = \left| \frac{n_1^\infty}{b_1} \cdot \frac{\theta}{1-\theta} \right| \exp \left| \frac{\alpha_{1v}^2 \theta}{1 + \alpha_{1v}\theta} \right| \tag{2}$$

where θ ($=n_1/n_1^\infty$) is the surface coverage.

Danner and his co-workers suggested that the temperature dependence of these parameters can be expressed in the following forms:

$$b_1 = b_{01} \exp \left(-\frac{q_1}{RT} \right) \tag{3}$$

$$n_1^\infty = n_{01}^\infty \exp \left(\frac{r_1}{T} \right) \tag{4}$$

and

$$\alpha_{1v} = m_1 n_1^\infty - 1 \tag{5}$$

where b_{01}, n_{01}^∞, q_1, r_1 and m_1 are assumed to be independent of temperature. b_1 (mmol/g·Torr) is the Henry's law constant of the adsorbate, n_1^∞ (mmol/g) is the limiting amount adsorbed, r_1 (°K) is a temperature-independent constant characterizing adsorbate-adsorbent system, α_{1v} is a parameter describing the nonideality in adsorbed phase induced by interaction between adsorbate and vacancy, q_1 (KJ/mol) is the isosteric heat of adsorption at infinite dilution, m_1 (g/mmol) is a temperature-independent constant of proportionality, R (KJ/mol·°K) is the gas constant, and T (°K) is the temperature of adsorption.

As cautioned by the authors, one should not attach too much physical significance to the regressed parameters although the model was developed by analogy with the Flory-Huggins model (20) for vapor-liquid equilibria. The authors further suggested that the parameters could either be computed using Eq. (2) for n_1^∞, b_1

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and α_{1v} or using Eq. (2), (3), (4), and (5) together with isotherms at different temperatures. In the present study, Eq. (2) was used to obtain n_1^∞, b_1 and α_{1v} from the experimental adsorption data at one temperature and a least square error regression method. The computer program is listed in Appendix B.

Both Langmuir and VSM isotherm equations were used to describe the adsorption of gases on 3A and 5A molecular sieve carbons in the present study. Both equations were employed to fit all the experimental data in the entire pressure range of 0-10,000 Torr obtained under this contract. The Langmuir constants for all the gases studied are tabulated in Table 2 while the parameters for the VSM are shown in Table 3.

TABLE 2. LANGMUIR EQUATION CONSTANTS

MSC	Gas	0°C		30°C		50°C	
		q_m mmol/g	b 1/Torr	q_m mmol/g	b 1/Torr	q_m mmol/g	b 1/Torr
3A	N_2	1.90	7.84×10^{-4}	1.97	3.34×10^{-4}	1.68	3.44×10^{-4}
	O_2	2.32	7.58×10^{-4}	2.01	3.08×10^{-4}	1.37	4.53×10^{-4}
	CH_4	3.23	7.81×10^{-4}	2.72	1.43×10^{-3}	2.01	1.11×10^{-3}
	Ar	2.38	4.61×10^{-4}	2.02	3.72×10^{-4}	1.61	3.03×10^{-4}
5A	N_2	2.08	7.44×10^{-4}	2.14	2.95×10^{-4}	1.58	3.65×10^{-4}
	O_2	2.42	5.25×10^{-4}	2.78	1.69×10^{-4}	1.64	2.87×10^{-4}
	CH_4	3.12	1.83×10^{-3}	2.62	7.47×10^{-4}	2.35	7.02×10^{-4}
	Ar	2.62	4.12×10^{-4}	1.81	4.06×10^{-4}	2.58	1.26×10^{-4}

P: pressure, Torr
q: adsorption capacity, mmol/g

Adsorption on 5A and 3A MSC

Adsorption of O_2 Both the low pressure adsorption unit and the high pressure adsorption unit were used to study the adsorption of O_2 on 5A MSC at 30°C. For low pressure runs, O_2 was adsorbed on a 5A sample previously activated at 300°C for 6 hours. The amount adsorbed at equilibrium was measured after a step increase in the adsorbate pressure. The data are shown by circles in Figure 7. Adsorption was rapid and equilibrium was achieved quickly as shown in Figures 8 and 9. (The differences in the figures were perhaps due to the differences in the sensitivity between the two apparatuses.) When the adsorption experiment was repeated using the sample that was not activated, but was desorbed completely of O_2 under vacuum (less than 10^{-4} Torr), the adsorption data (squares in Figure 7) were reproducible. O_2 was

TABLE 3. ISOTHERM PARAMETERS FOR THE VACANCY SOLUTION MODEL

MSC	Gas	Temp(°C)	Parameters of VSM		
			n_1^∞ (mmol/g)	b_1 (mmol/g·Torr)	α_{1v}
3A	N_2	0	2.1183	1.0982×10^{-3}	-3.26×10^{-11}
		30	1.9893	0.6606×10^{-3}	-3.28×10^{-12}
		50	1.8188	0.5321×10^{-3}	-7.14×10^{-11}
	O_2	0	2.6571	1.3865×10^{-3}	2.31×10^{-12}
		30	2.3844	0.5315×10^{-3}	-1.13×10^{-12}
		50	1.7375	0.4899×10^{-3}	3.92×10^{-10}
	CH_4	0	3.6728	2.0124×10^{-3}	-2.24×10^{-11}
		30	2.7504	3.7574×10^{-3}	-1.31×10^{-11}
		50	2.0496	2.1960×10^{-3}	-1.14×10^{-11}
	Ar	0	2.6080	0.9472×10^{-3}	1.57×10^{-11}
		30	2.2170	0.6175×10^{-3}	9.01×10^{-14}
		50	1.8223	0.4318×10^{-3}	-1.06×10^{-12}
5A	N_2	0	2.4625	1.1330×10^{-3}	-1.82×10^{-11}
		30	2.3531	0.5725×10^{-3}	8.14×10^{-12}
		50	1.9027	0.4723×10^{-3}	1.44×10^{-11}
	O_2	0	2.8299	1.0380×10^{-3}	-1.51×10^{-11}
		30	2.8468	0.4654×10^{-3}	3.29×10^{-10}
		50	2.2330	0.3959×10^{-3}	-3.26×10^{-11}
	CH_4	0	3.3112	4.7407×10^{-3}	-8.32×10^{-12}
		30	3.0366	1.5465×10^{-3}	-7.64×10^{-11}
		50	2.6299	1.4269×10^{-3}	-1.23×10^{-11}
	Ar	0	2.8879	0.9260×10^{-3}	-7.51×10^{-11}
		30	2.1067	0.6026×10^{-3}	-2.83×10^{-12}
		50	2.8535	0.3075×10^{-3}	-2.34×10^{-11}
BF^a	N_2	30	1.5902	0.3831×10^{-3}	-1.03×10^{-11}
	O_2	30	1.7429	0.5270×10^{-3}	-9.46×10^{-12}
	CH_4	30	1.7781	1.6974×10^{-3}	1.39×10^{-11}
	Ar	30	1.8889	0.3544×10^{-3}	1.76×10^{-11}

^{a} BF = Bergbau Forschung

easily desorbed. Figure 7 shows that both the adsorption and the desorption isotherms are fairly linear below 760 Torr. In Figure 10, data obtained using the low-pressure unit were plotted together with those obtained using the high-pressure unit. The excellent agreement between the data obtained from the low pressure unit and those from the high pressure unit is a good indication of the consistency of the adsorption data. Similar observations were made for O_2 on 3A MSC as shown in Figure 11. Figures 12 and 13 are the adsorption isotherms at 0°C, 30°C, and 50°C for O_2 on 5A and 3A MSC, respectively.

Adsorption of CH_4 Following O_2 adsorption on 5A MSC and subsequent complete desorption under vacuum, CH_4 was adsorbed. The amount adsorbed at equilibrium is shown in Figure 14 using

13
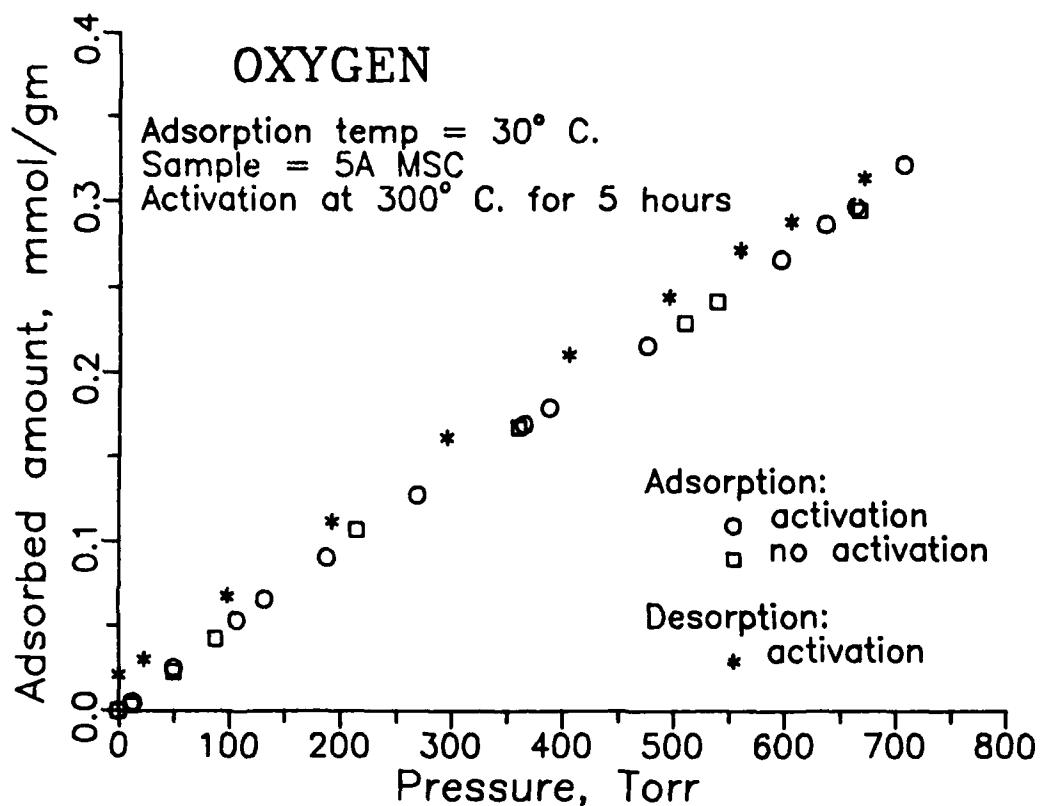
Figure 7. O_2 adsorption and desorption isotherms.
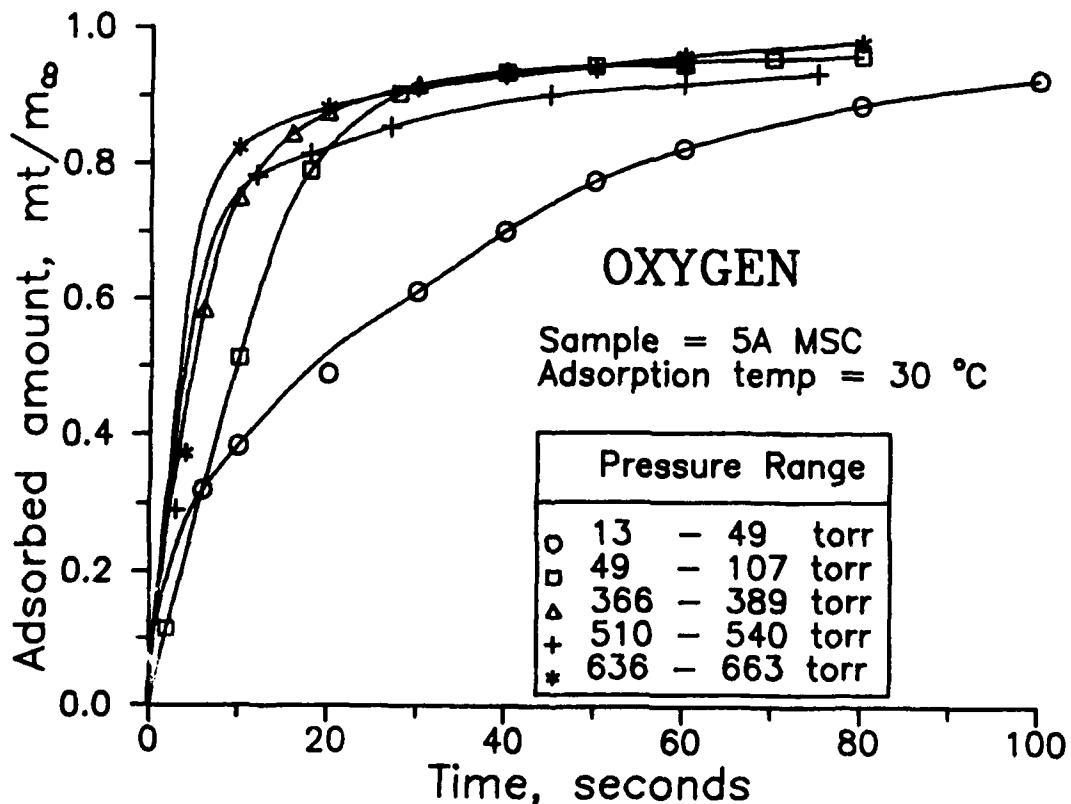
Figure 8. Uptake curves during O_2 adsorption (low pressure).

14
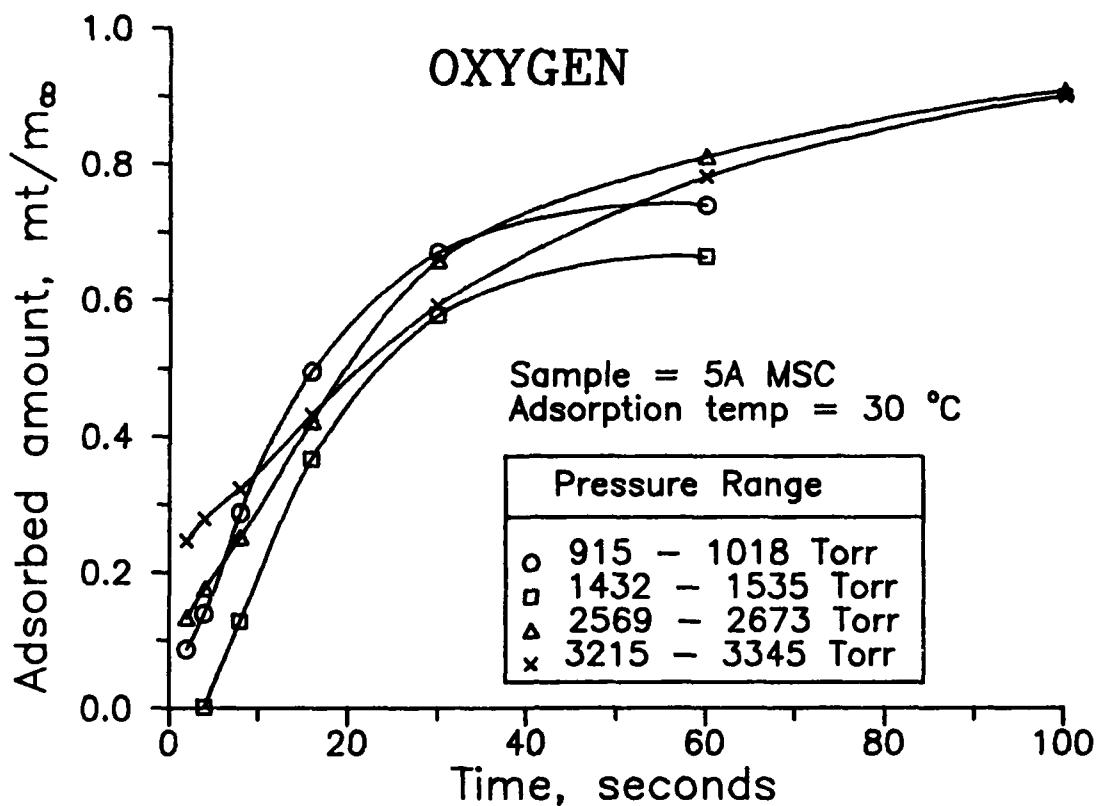
Figure 9. Uptake curves during O_2 adsorption (high pressure).
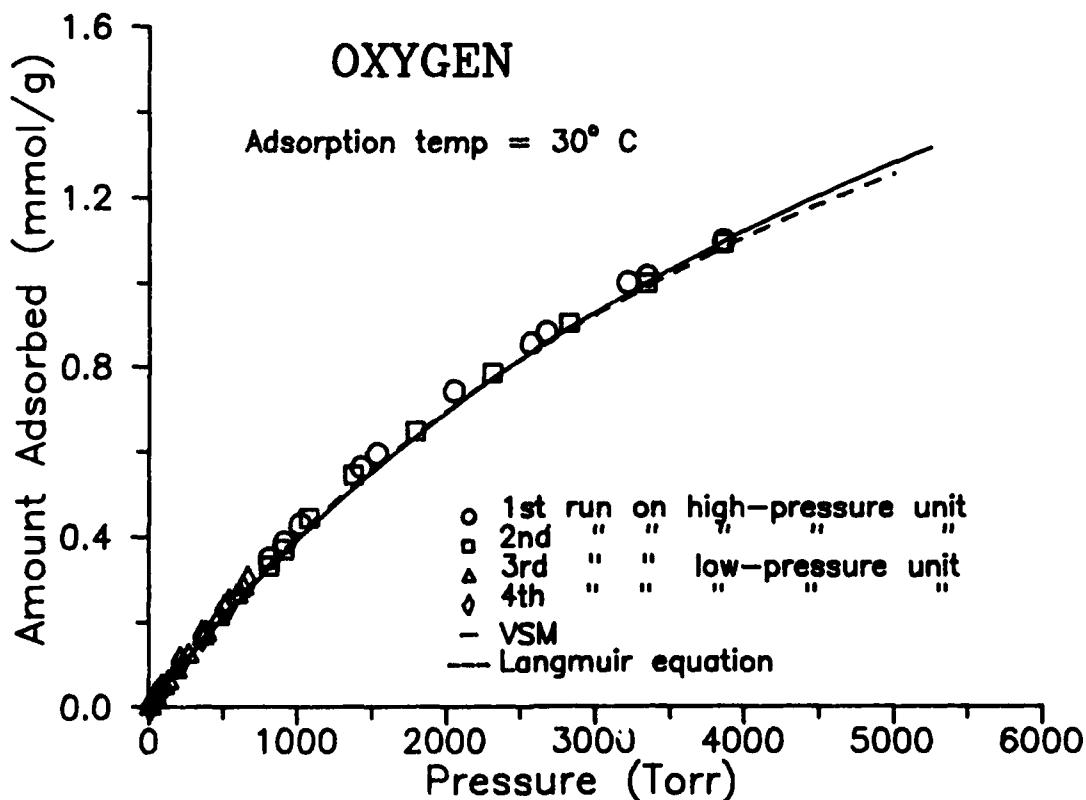
Figure 10. O_2 adsorption isotherm on 5A MSC.

15
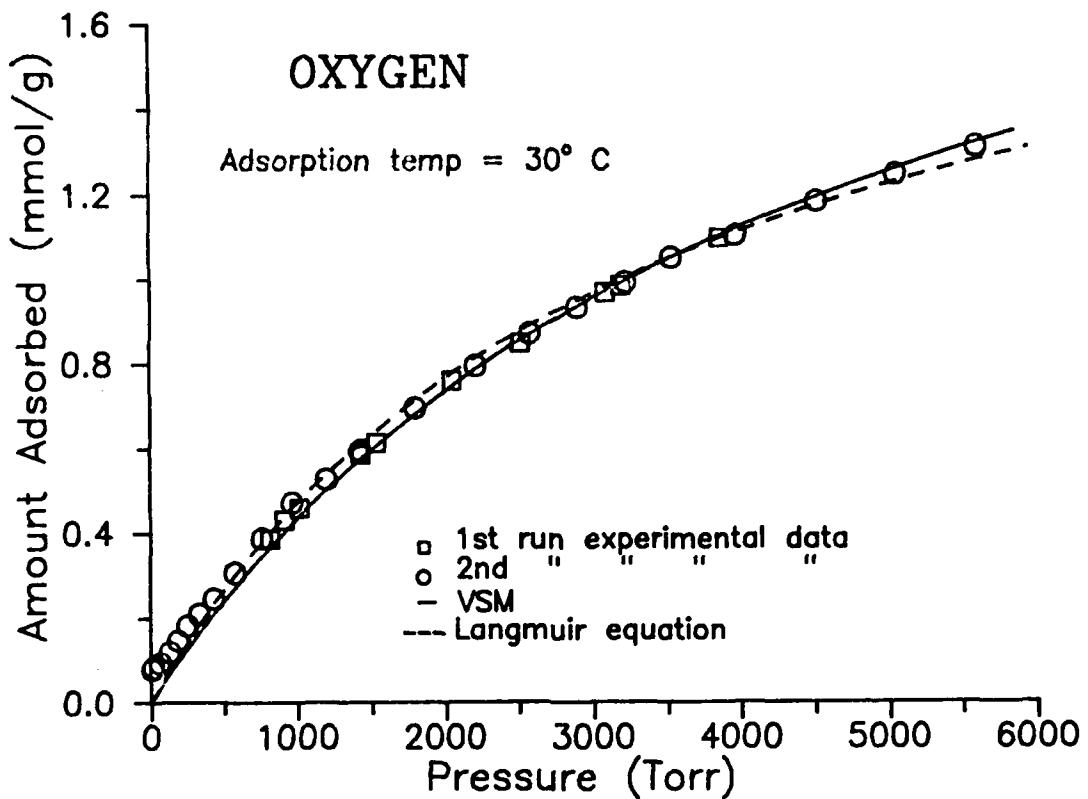
Figure 11. O_2 adsorption isotherm on 3A MSC.
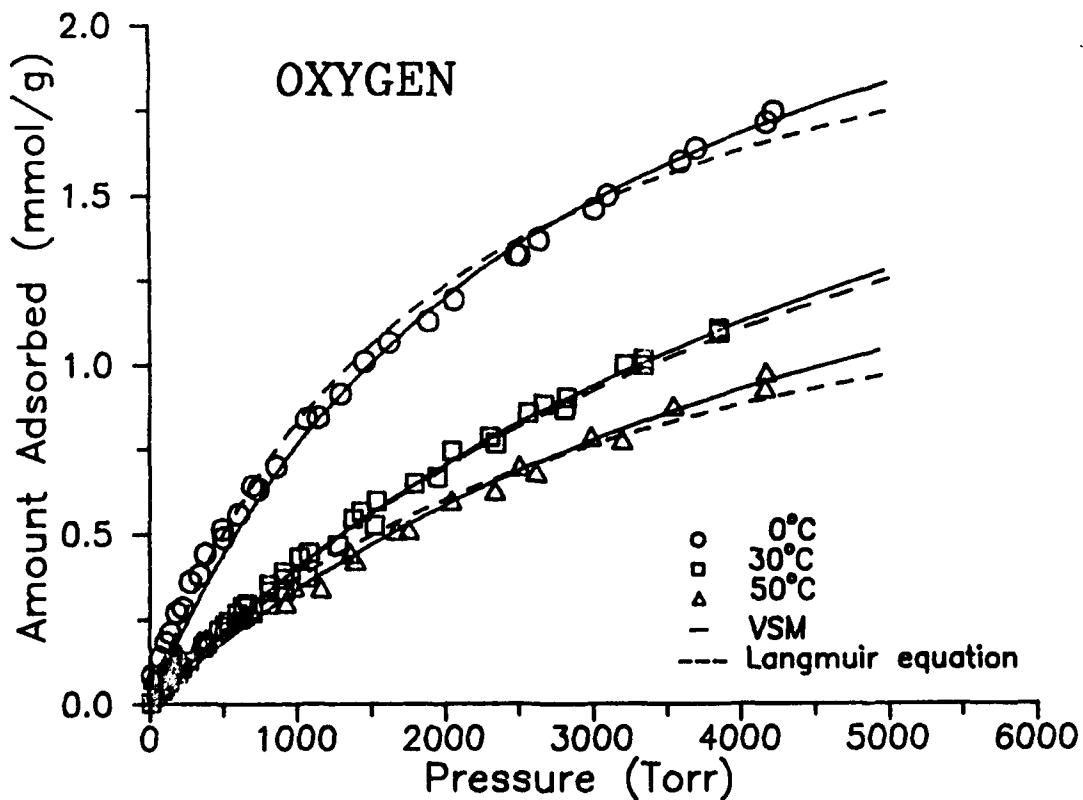
Figure 12. O_2 adsorption isotherm on 5A MSC.
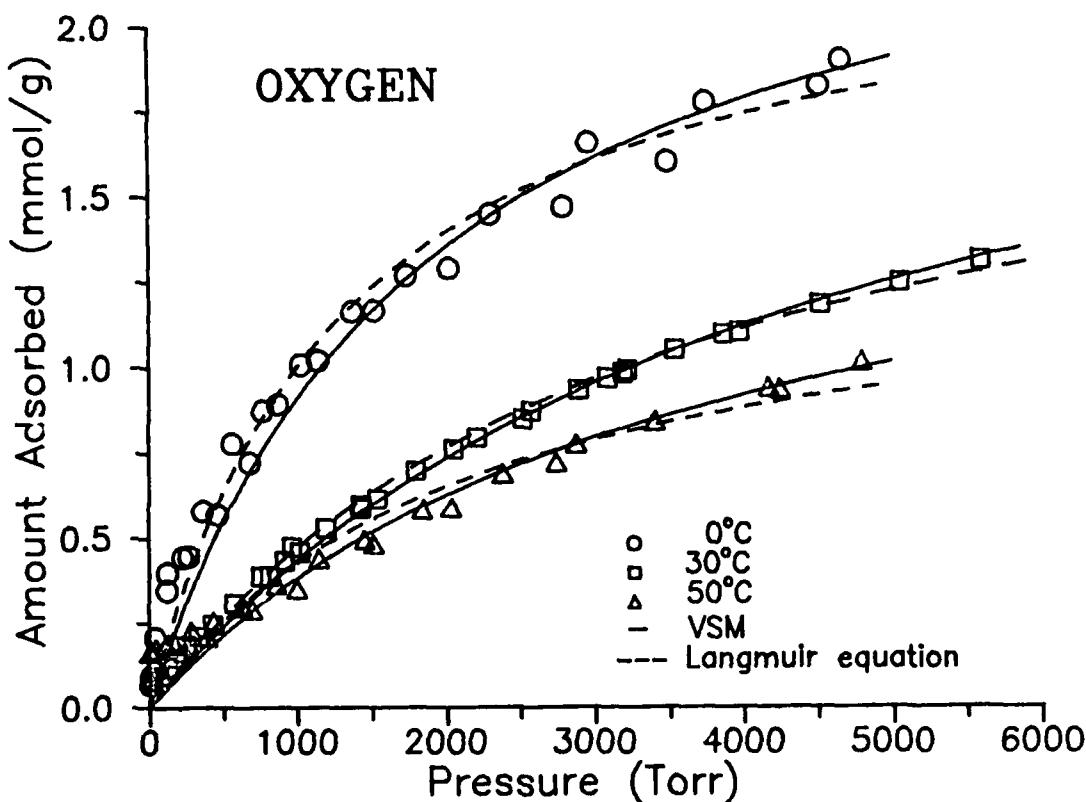
Figure 13. O_2 adsorption isotherm on 3A MSC.
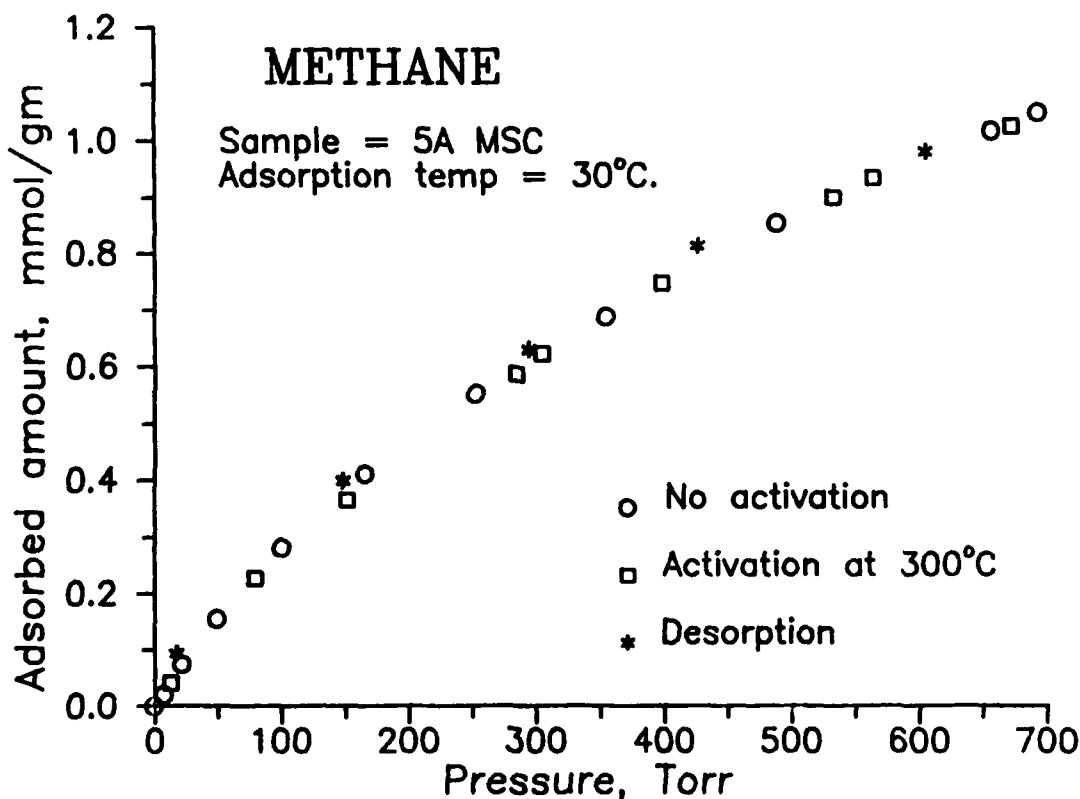
Figure 14. CH_4 adsorption and desorption isotherm on 5A MSC.
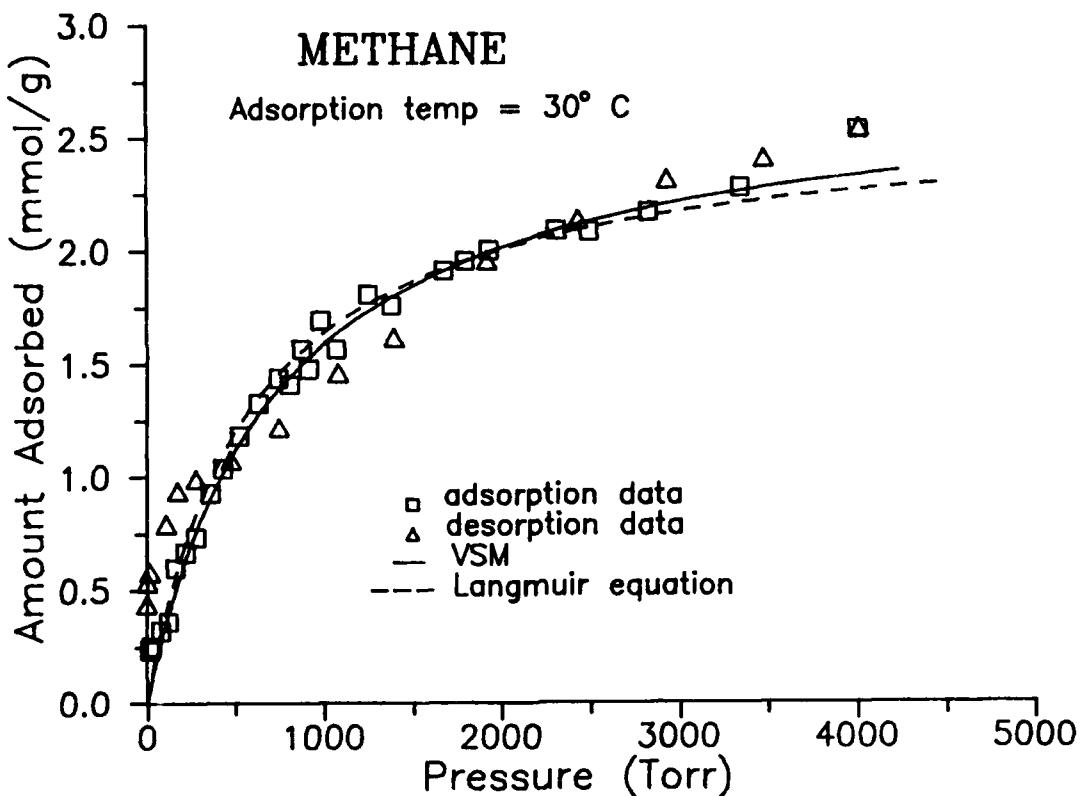
Figure 15. CH₄ adsorption and desorption isotherm on 3A MSC.

circles. Adsorption capacity of the sample was the same when it was activated at 300°C for 6 hours prior to CH₄ adsorption.

At low pressures, the desorption isotherm closely followed the adsorption isotherm as shown in Figure 14. It should, however, be pointed out that it was not possible to obtain complete desorption after the sample had been exposed to high pressure gas as shown in Figure 15. At high pressures, gas molecules may be adsorbed in the finer pores of the MSC making it difficult to desorb without heating. In Figure 16 the data obtained in the low-pressure unit and the high-pressure unit are shown. A similar curve for 3A MSC is shown in Figure 17. The adsorption equilibrium isotherms for CH₄ in 5A and 3A MSC are shown in Figures 18 and 19 respectively at three temperatures, 0°C, 30°C, and 50°C. The behavior of methane adsorption isotherms on 3A was unusual. The equilibrium adsorption capacity at 30°C was higher than at 0°C at pressures less than 2,500 Torr. One possible explanation for this variation is that the adsorption rate for methane at 0°C was very low and equilibrium was never reached. More work is needed to fully understand this apparent anomaly.

Adsorption of N₂ Adsorption of N₂ on 5A MSC was also checked using the sample that was activated at 300°C for 6 hours, and the sample that was simply desorbed of CH₄ but not activated. In both cases the adsorption isotherms were identical. Further, the

18
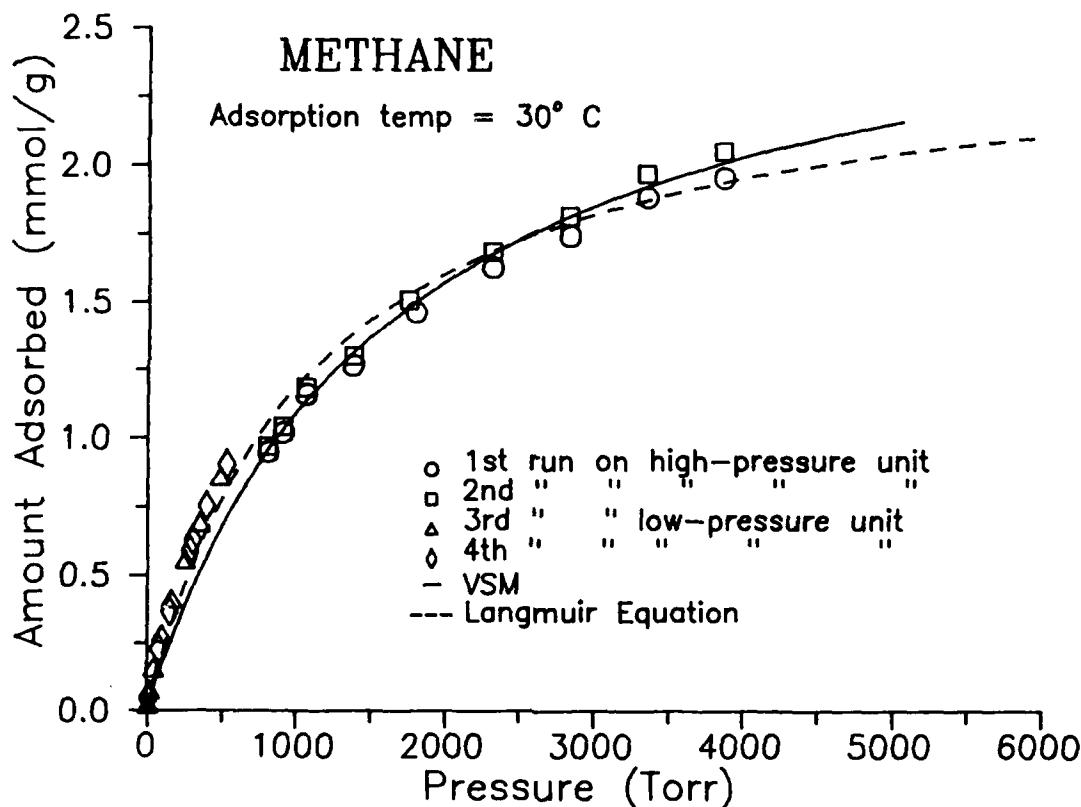
Figure 16. CH_4 adsorption isotherm on 5A MSC.
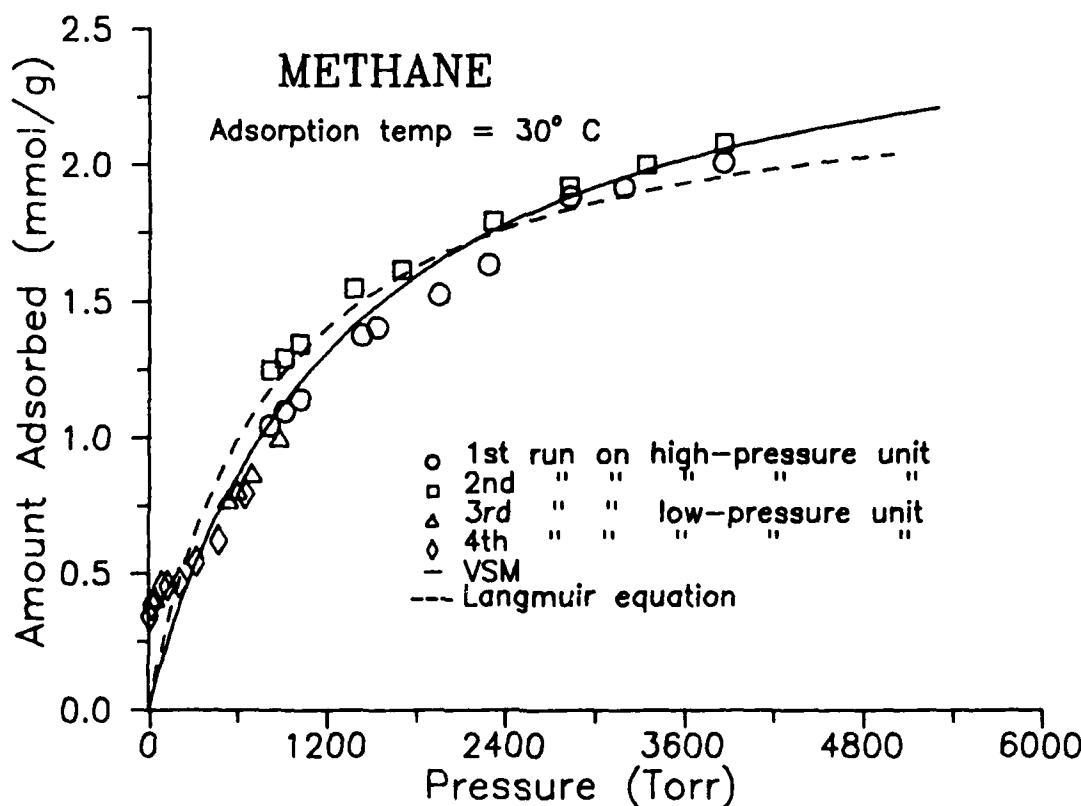
Figure 17. CH_4 adsorption isotherm on 3A MSC.
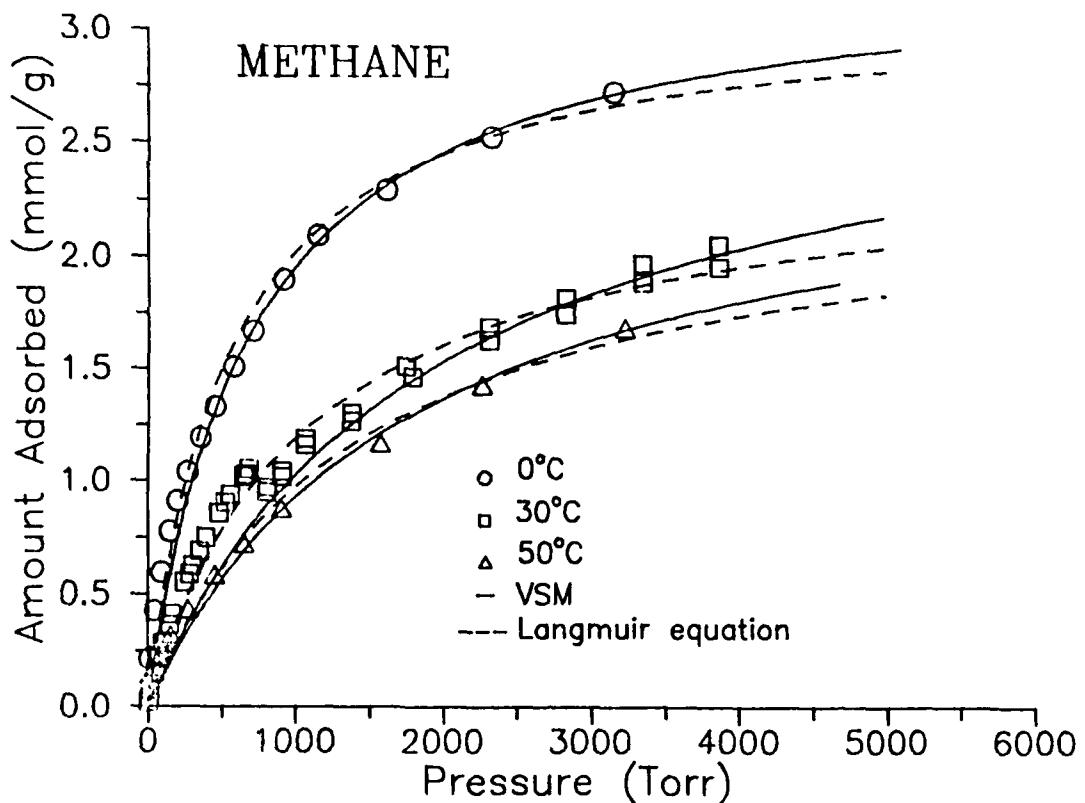
Figure 18. CH_4 adsorption isotherm on 5A MSC.
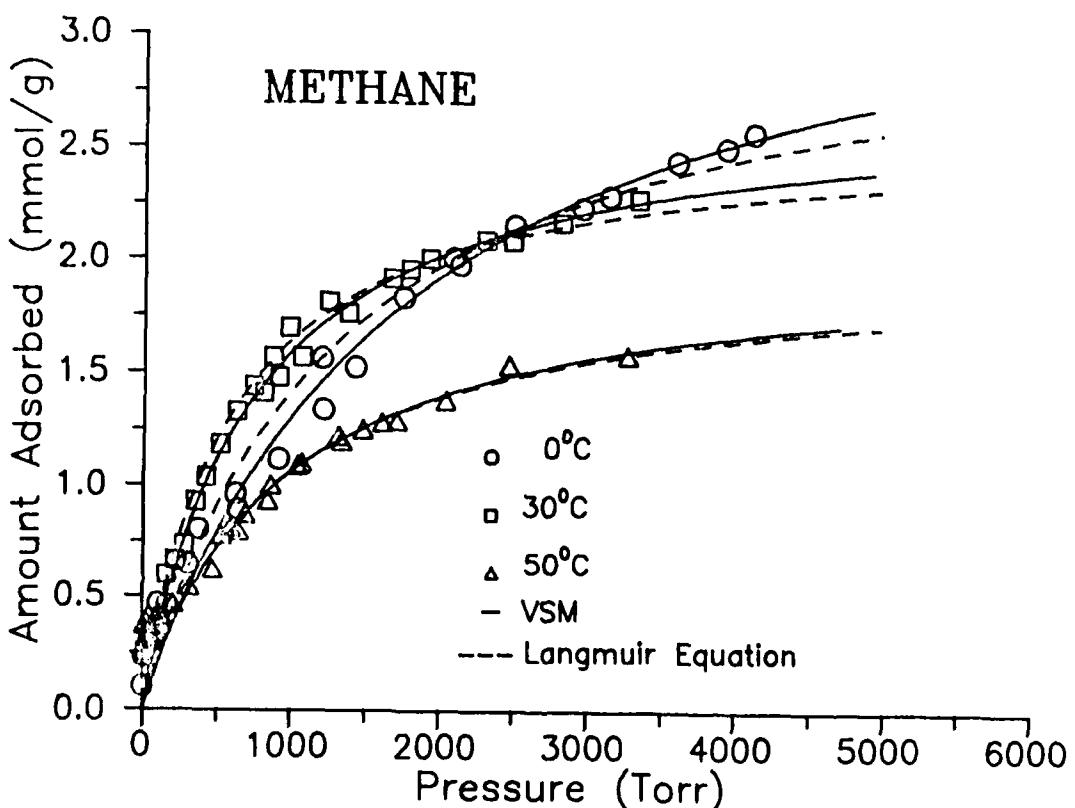
Figure 19. CH_4 adsorption isotherm on 3A MSC.

desorption isotherm was similar to the adsorption isotherm.
These data are shown in Figure 20. The adsorption data over the
entire pressure range of 0-6,000 Torr are shown in Figure 21.
The adsorption equilibrium isotherms for N_2 in 5A and 3A MSC are
shown in Figures 21 and 22 respectively at three temperatures,
0°C, 30°C, and 50°C.

Adsorption of Ar Figures 23 and 24 show the equilibrium
adsorption isotherms for argon in 5A and 3A MSC at three
temperatures, 0°C, 30°C, and 50°C. The VSM appears to give a
good fit of the experimental data. The Langmuir equation seems
to be adequate for the description of the isotherms although some
deviation of the experimental data from the theoretical curve was
observed at high pressures.

Comparison with previous studies There are relatively few
studies providing equilibrium adsorption isotherms for molecular
sieve carbons. Materials from different sources make it even
more difficult to make an accurate comparison. Nevertheless,
Figure 25 compares the current results for 5A MSC and those
reported by Ruthven et al. (24). Although there are some
differences between the present study and that of Ruthven et al,
the agreement should be regarded as fairly good considering the
substantial differences among the materials. Kapoor and Yang
(25) found that the adsorption data for methane could be fitted
using a Langmuir equation for Bergbau Forschung molecular sieve
carbon at 25°C. They obtained a q_m value of 1.92 mmol/g and a b
value of $8x10^{-4}$ $Torr^{-1}$ which are somewhat different from the
results in Table 2. However, considering the fact that the
materials used in Kapoor and Yang's work were from Bergbau
Forschung, the observed differences probably would be expected.

Additional experiments were performed on the MSC produced by
Bergbau Forschung for comparison. The results are shown in
Figures 26, 27, 28 and 29 for methane, oxygen, nitrogen and
argon, respectively. From these figures, it appears that the 3A
MSC from Takeda had, in general, higher capacities than those of
Bergbau Forschung.

Isosteric Heat of Adsorption

The temperature dependence of adsorption isotherms can be
used to derive the isosteric heat of adsorption which is a
differential molar quantity. The derivation of an equation for
the isosteric heat of adsorption is similar to the derivation of
the Clausius-Clapeyron equation for a phase change in a one-
component system. Therefore, the equation for the isosteric heat
of adsorption is:

$$\left. \frac{\partial (\ln P)}{\partial (1/T)} \right|_n = - \frac{q^{st}}{R} \qquad (6)$$

21
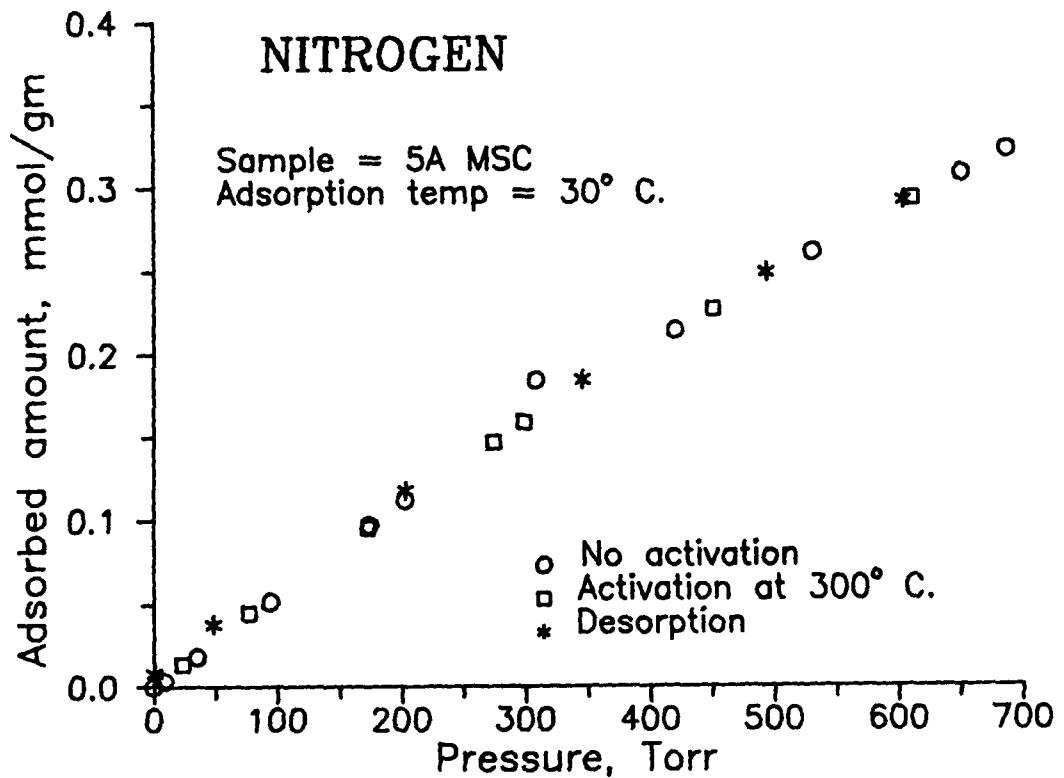
Figure 20. N_2 adsorption and desorption isotherm on 5A MSC.
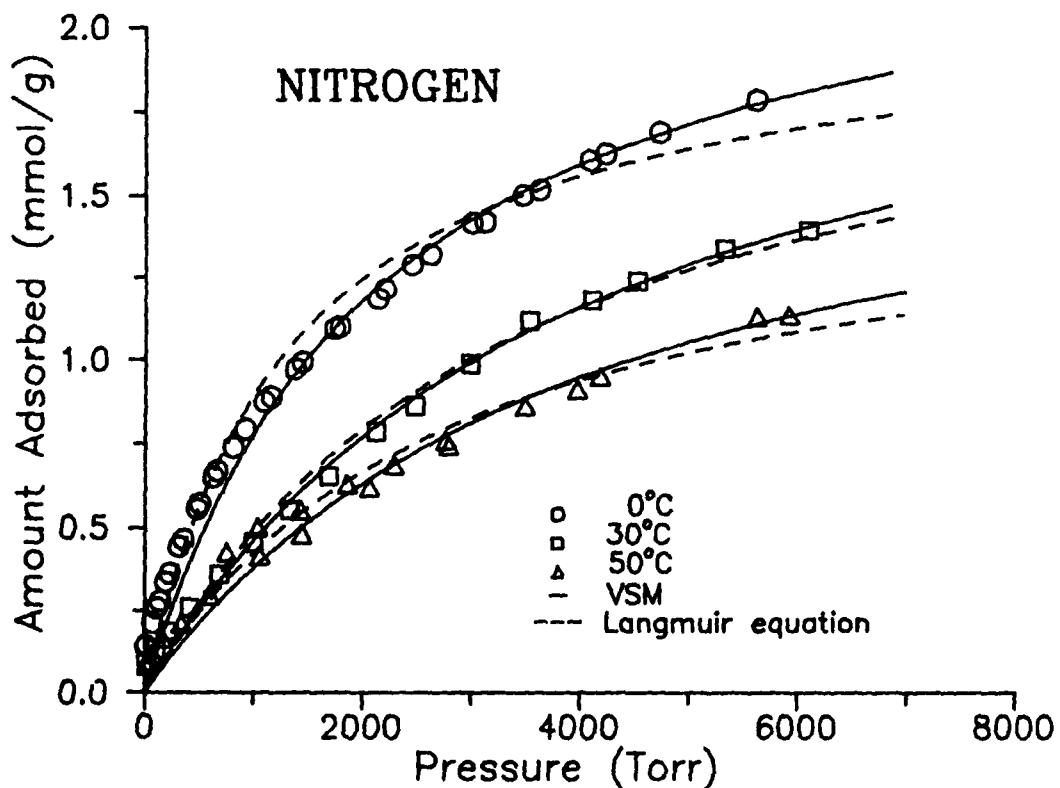
Figure 21. N_2 adsorption isotherm on 5A MSC.
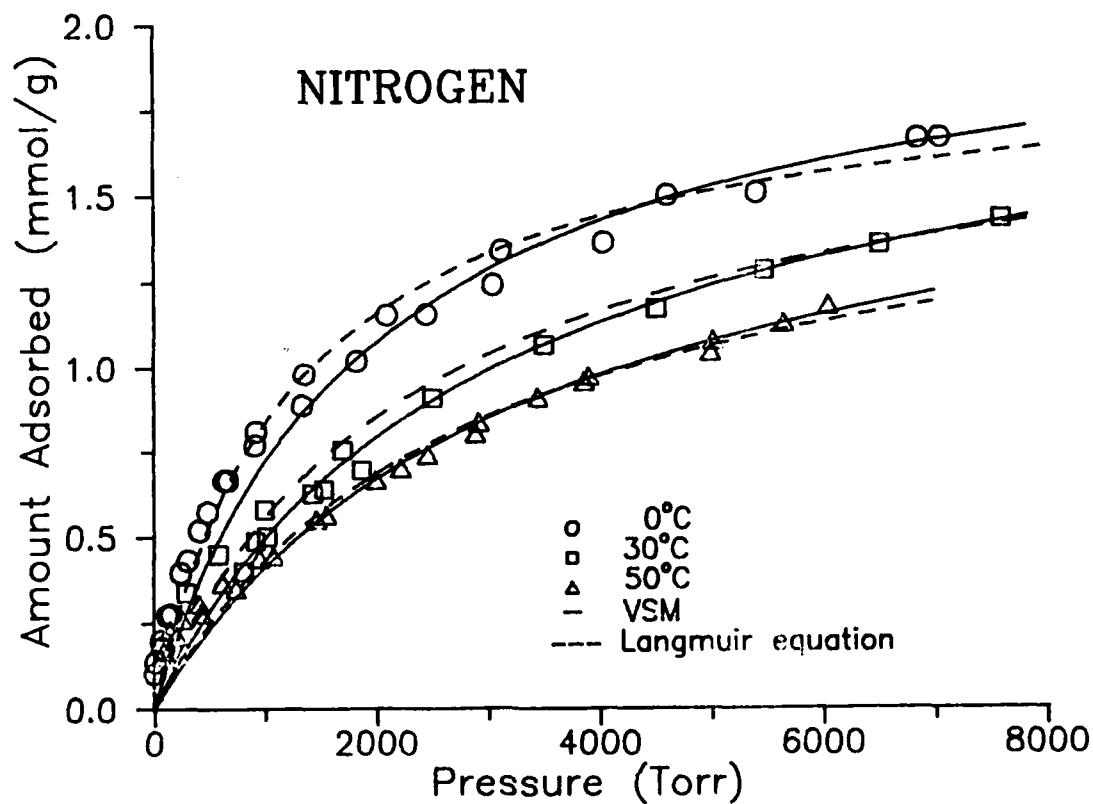
Figure 22. N_2 adsorption isotherm on 3A MSC.
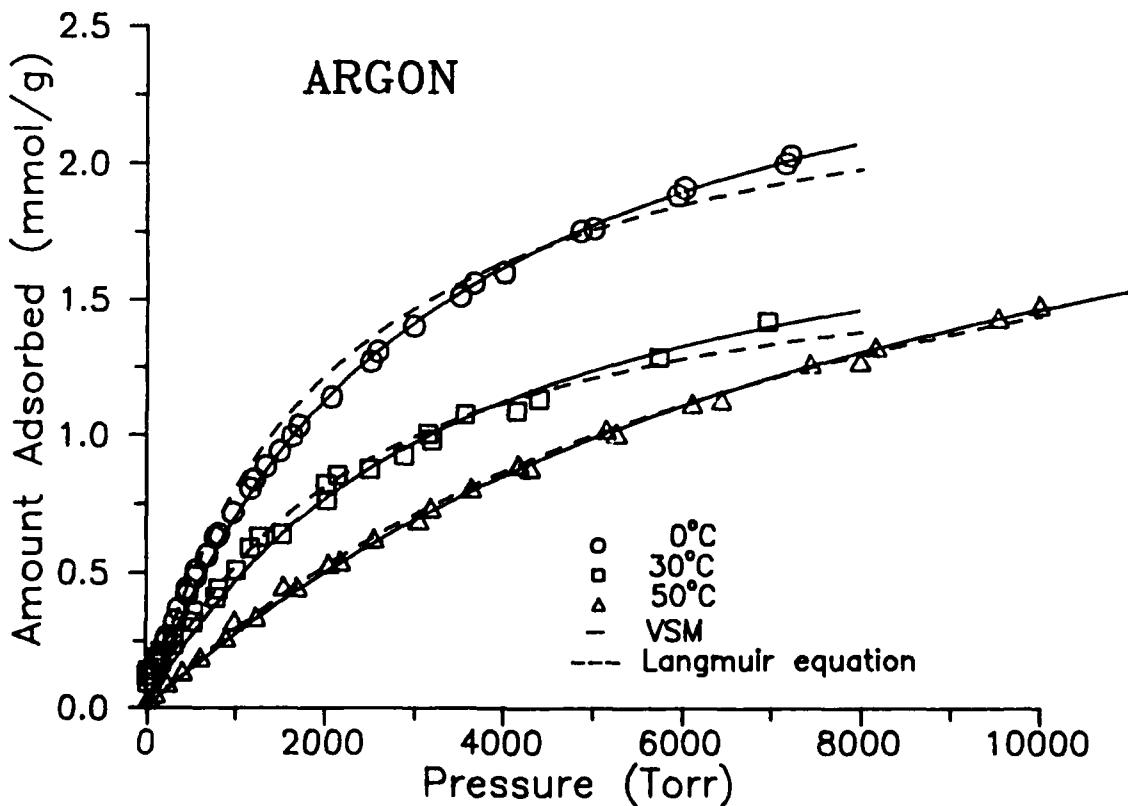
Figure 23. Ar adsorption isotherm on 5A MSC.

23
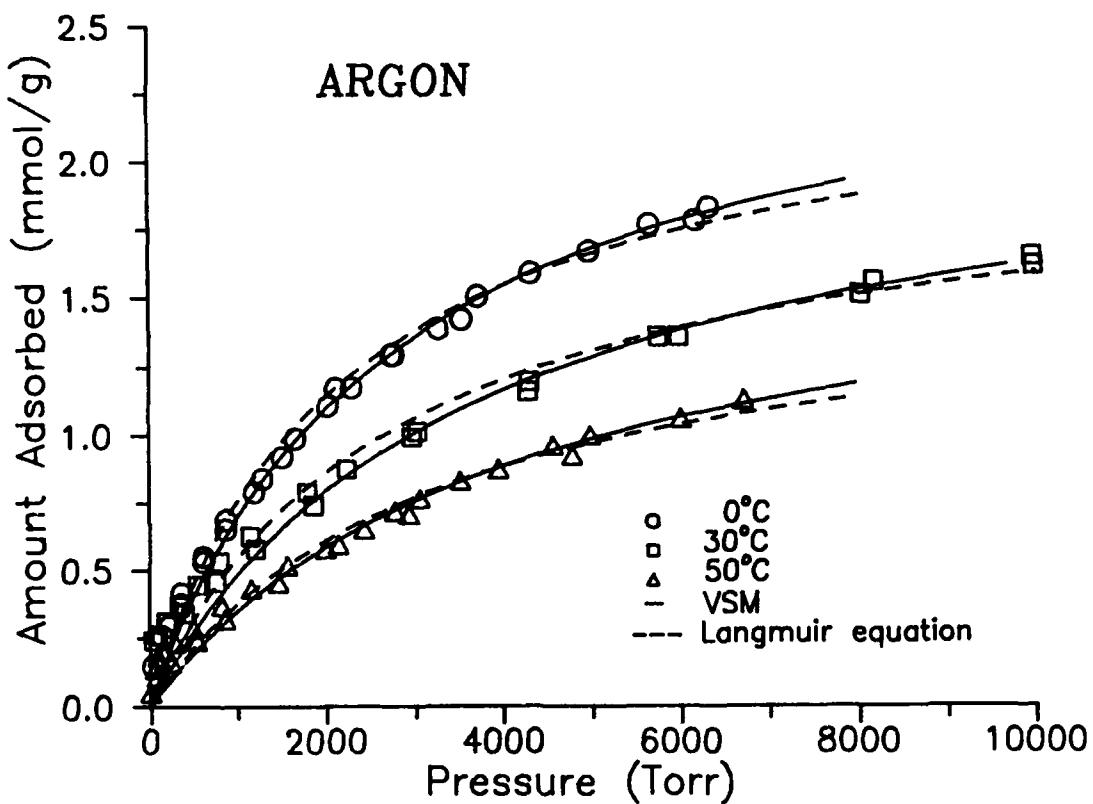
Figure 24. Ar adsorption isotherm on 3A MSC.
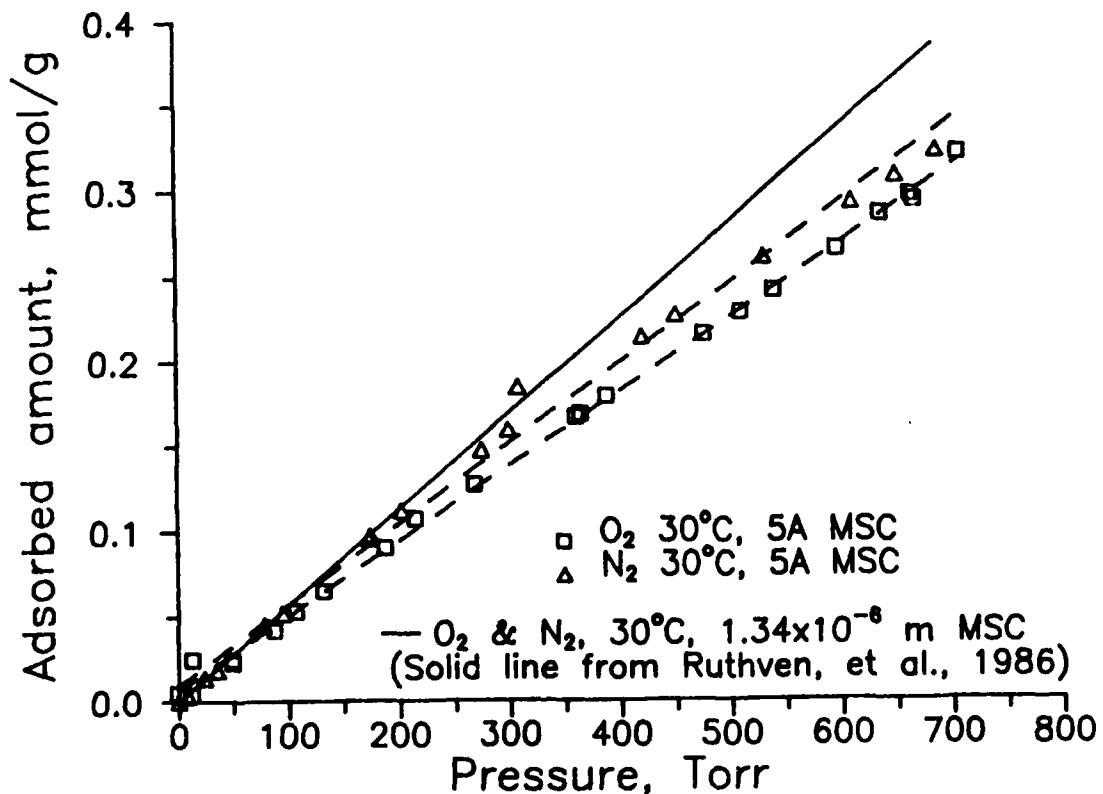
Figure 25. Adsorption capacities of different samples.
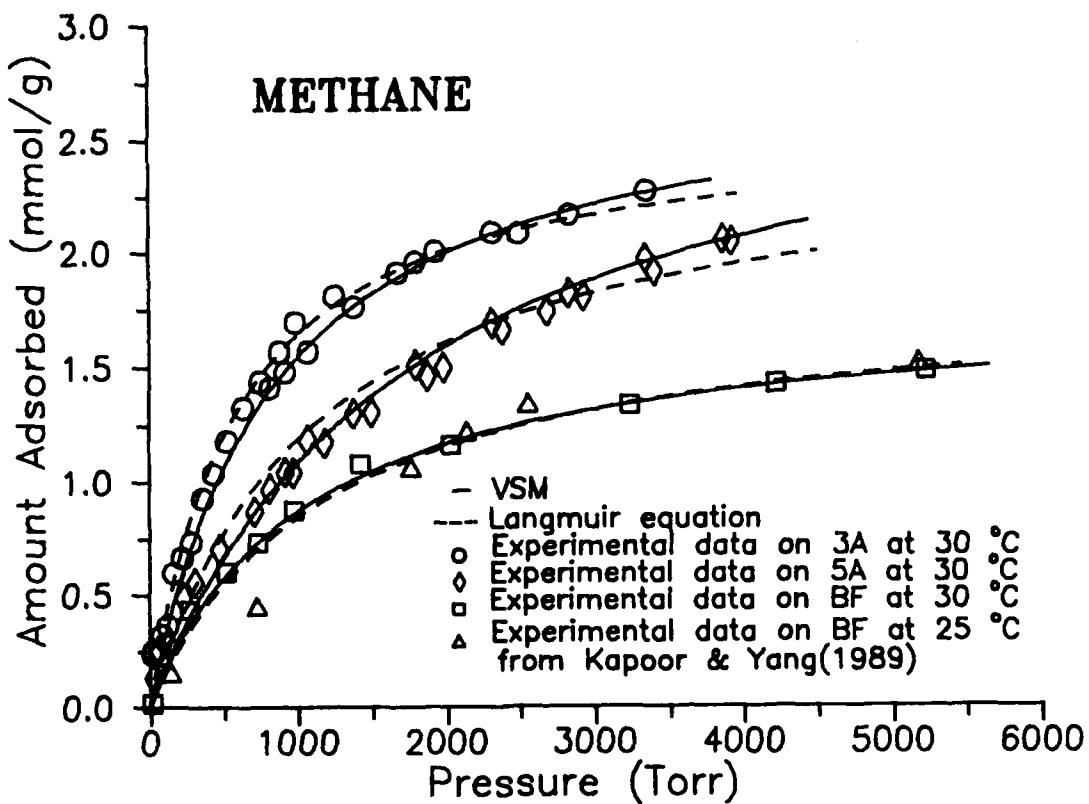
Figure 26.   CH$_4$ adsorption on various samples.
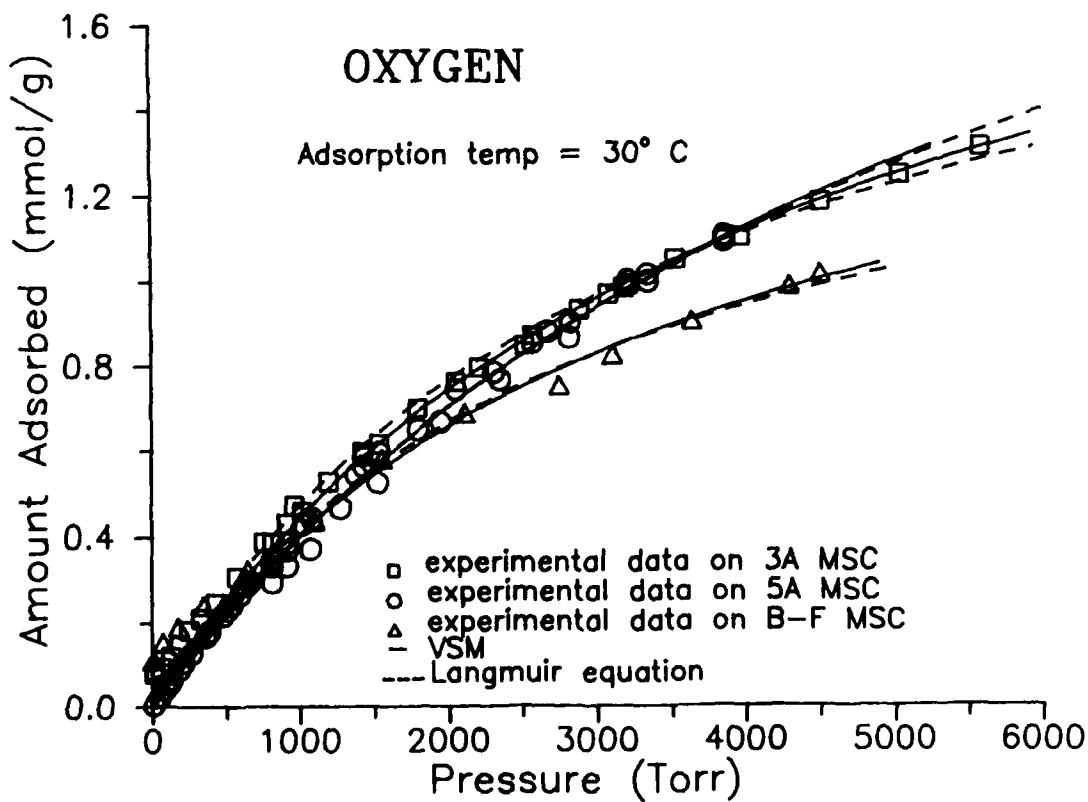
Figure 27.   O$_2$ adsorption on various samples.
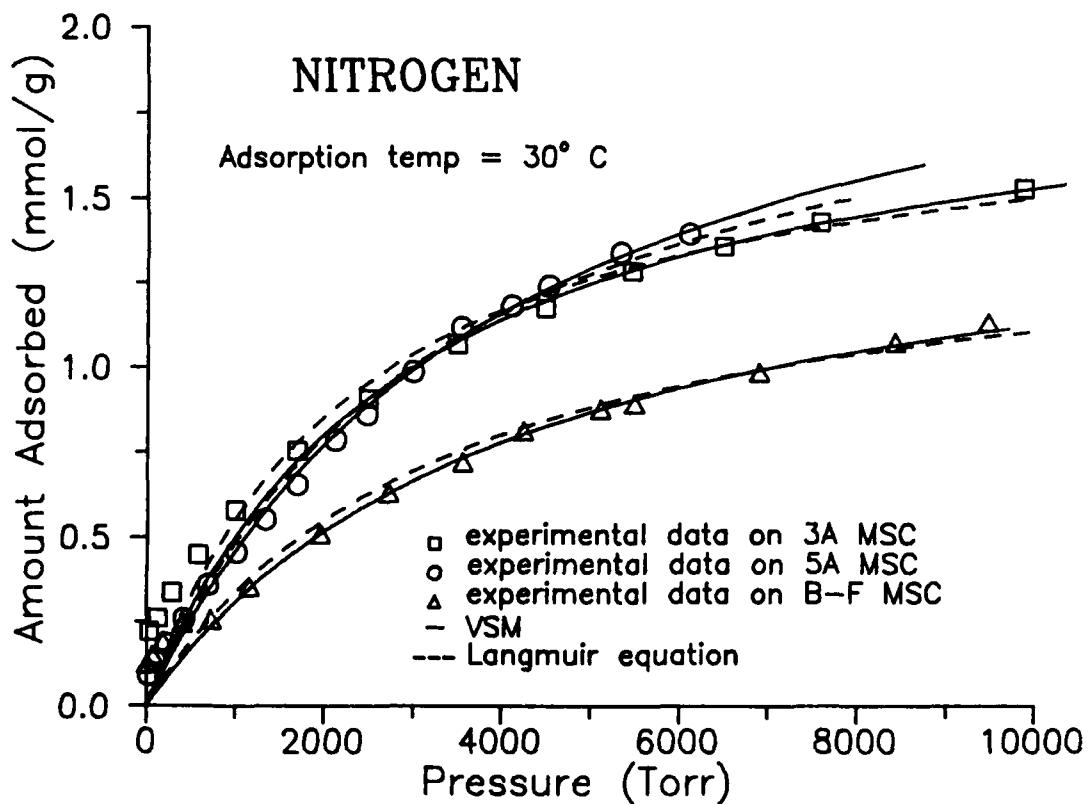
Figure 28. N_2 adsorption on various samples.
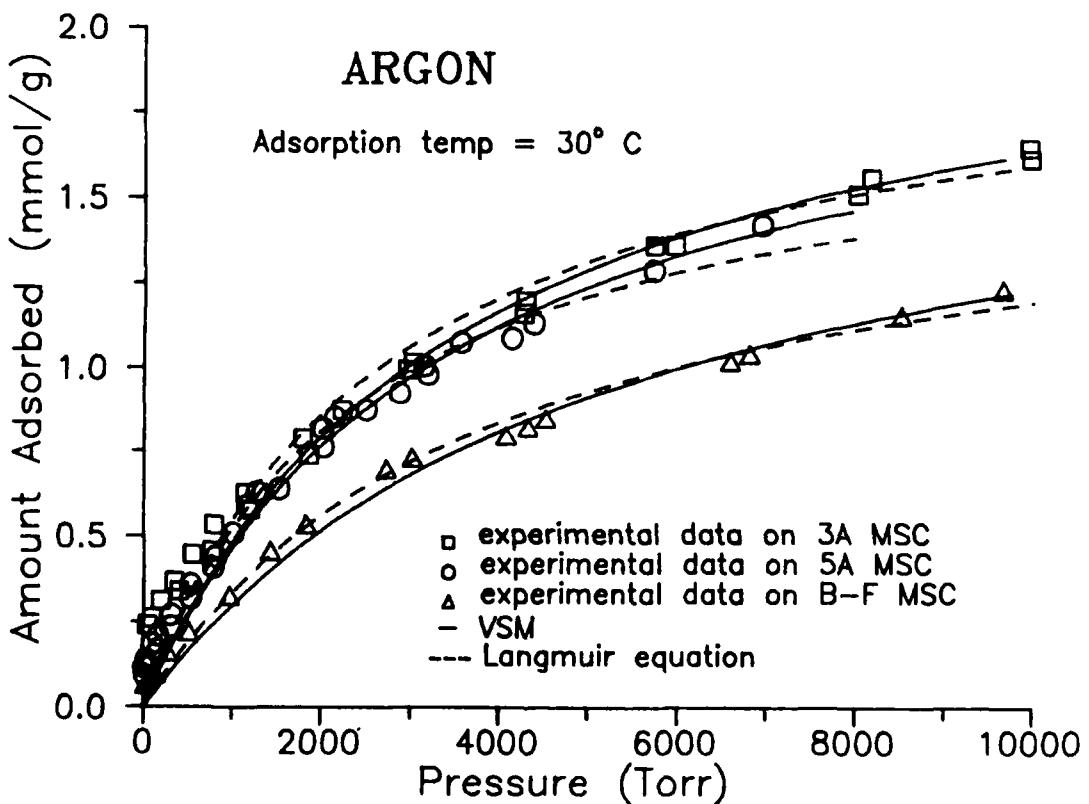
Figure 29. Ar adsorption on various samples.

where q^{st} is the isosteric heat of adsorption, R is the gas constant and n is the amount adsorbed.

From Eq. (6), it is clear that a plot of ln P vs 1/T at a constant adsorbed amount will yield a straight line with the slope of $-\dfrac{q^{st}}{R}$. Typical plots are shown in Figures 30 and 31 for argon on both 5A and 3A MSC. Straight lines are obtained for both cases. The isosteric heats of adsorption for all the gases studied are tabulated as a function of the amount adsorbed in Tables 4 and 5 for 5A and 3A MSC respectively and are plotted in Figure 32. It is seen that the values for methane are higher than for other gases. The difference between the values for 3A MSC and 5A MSC is the least in the case of nitrogen, and the most in the case of argon. Further, in the case of argon, the q^{st} values were considerably higher on 5A MSC than on 3A MSC. The

TABLE 4.   ISOSTERIC HEAT OF ADSORPTION FOR GASES ON 5A MSC

Gas: N_2		O_2		CH_4		Ar	
q^a mmol/g	$-q^{st\,b}$ KJ/mol	q mmol/g	$-q^{st}$ KJ/mol	q mmol/g	$-q^{st}$ KJ/mol	q mmol/g	$-q^{st}$ KJ/mol
0.046	12.92	0.055	14.73	0.056	16.31	0.036	15.67
0.114	13.19	0.139	15.01	0.139	16.49	0.089	15.71
0.228	13.69	0.277	15.54	0.278	16.84	0.179	15.79
0.456	14.99	0.554	16.94	0.556	17.66	0.357	15.97
0.684	16.96	0.831	19.10	0.834	18.76	0.536	16.18

a: q=amount adsorbed b: q^{st}=isosteric heat of adsorption

TABLE 5.   ISOSTERIC HEAT OF ADSORPTION FOR GASES ON 3A MSC

Gas: N_2		O_2		CH_4		Ar	
q^a mmol/g	$-q^{st\,b}$ KJ/mol	q mmol/g	$-q^{st}$ KJ/mol	q mmol/g	$-q^{st}$ KJ/mol	q mmol/g	$-q^{st}$ KJ/mol
0.035	13.12	0.042	17.33	0.534	18.11	0.036	10.99
0.089	13.23	0.104	17.57	0.133	18.38	0.091	11.18
0.177	13.43	0.208	18.02	0.267	18.88	0.182	11.55
0.355	13.92	0.417	19.12	0.534	20.05	0.364	12.41
0.532	14.59	0.625	20.63	0.801	21.57	0.547	13.52

a: q=amount adsorbed b: q^{st}=isosteric heat of adsorption
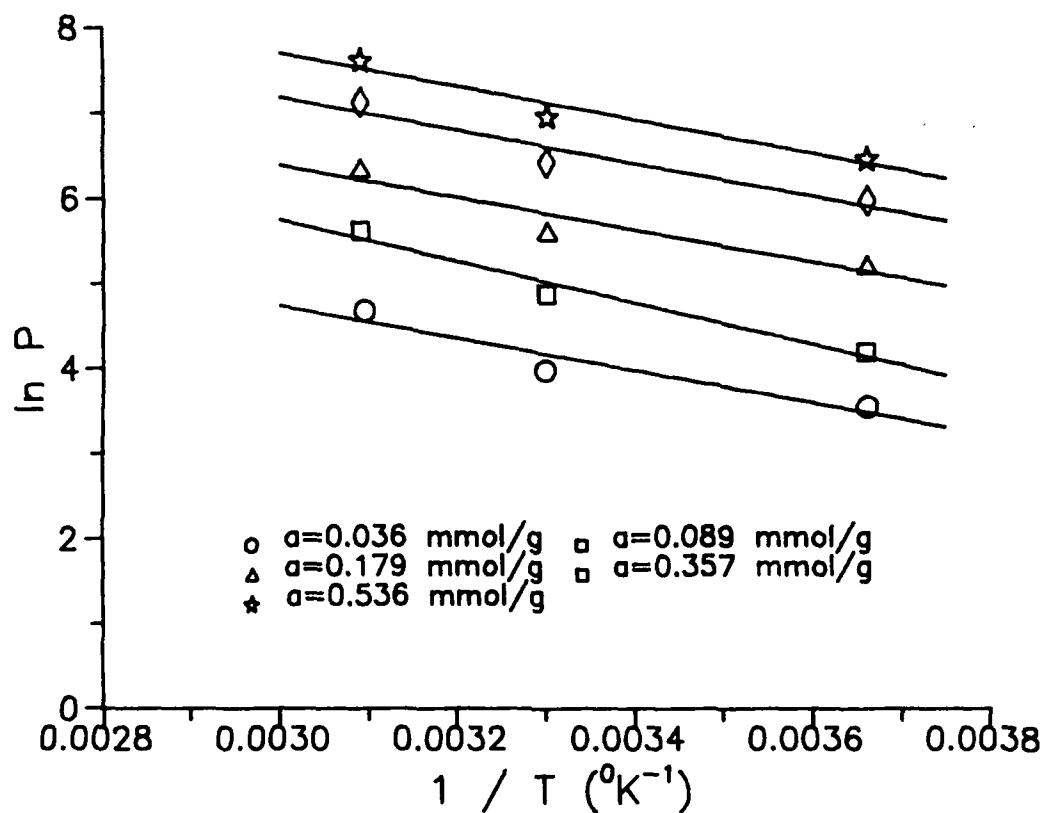
Figure 30.   Plot of (ln P) vs. (1/T) for Ar on 5A MSC.
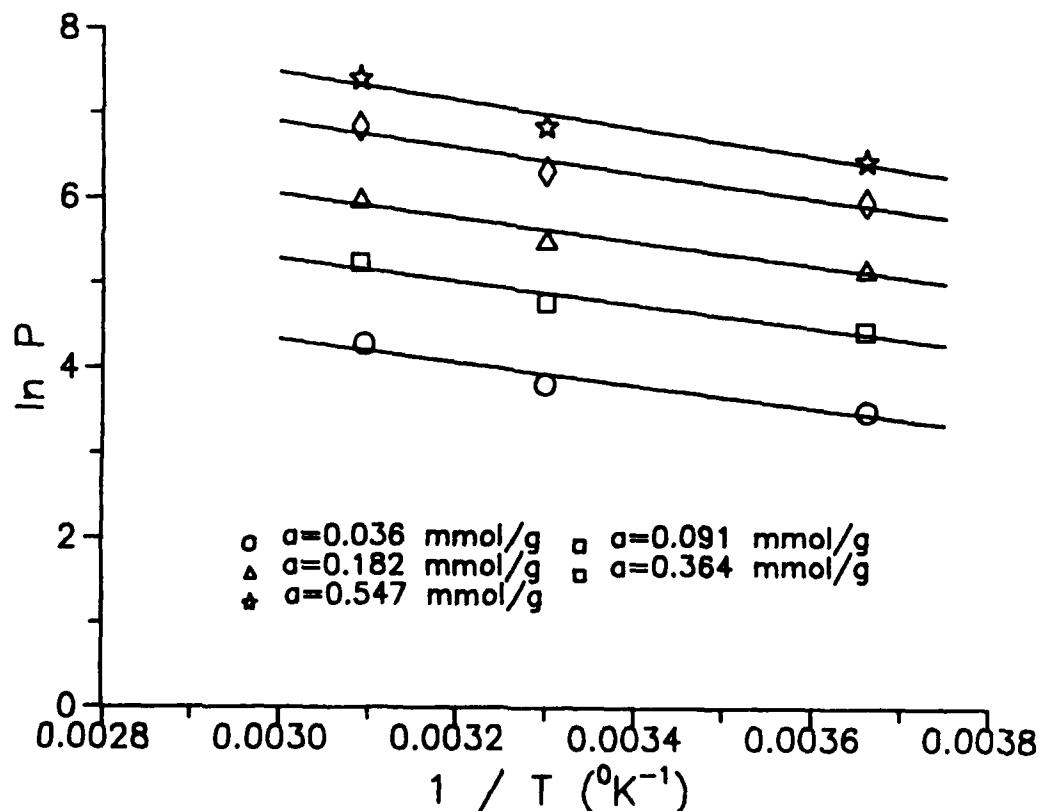
Figure 31.   Plot of (ln P) vs. (1/T) for Ar on 3A MSC.
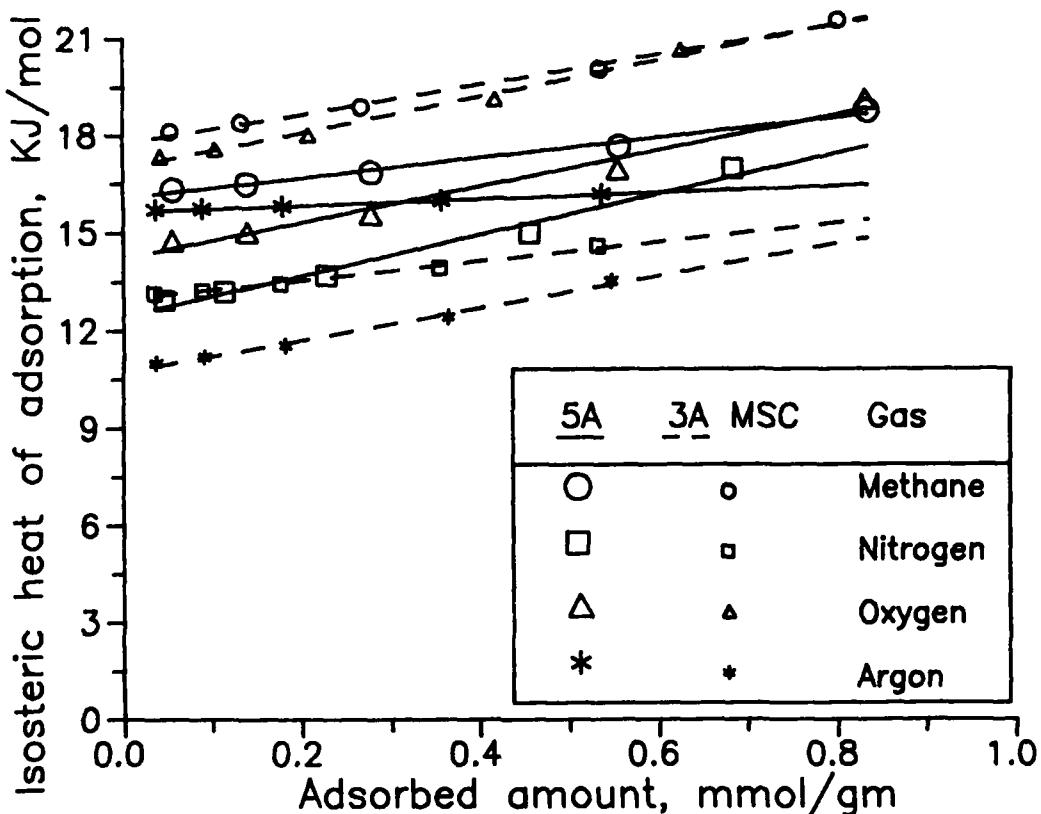
Figure 32.   Isosteric heat of adsorption vs. coverage.

reason for the high values is unclear at the present.   More work
is needed to clarify this point.

From the low surface coverage data reported by Chihara   et
al. (26) for 5A MSC, the q^{st} values were 18.8, 23.8 and 16.7
KJ/mol, respectively, for nitrogen, methane and argon.   Comparing
these values with those given in Table 4 we find that the values
obtained for methane and nitrogen in the present study are lower,
on an average, by about 30%.   The values for argon are close in
both studies.   The isosteric heat of adsorption which is a
measure of the interactions between adsorbate molecules and
adsorbent lattice atoms, may be used as a measure of the
energetic heterogeneity of a surface.   Observed differences in
the q^{st} values for the same gas on different samples point to the
differences in the nature of the sample surfaces.   (As already
noted, the reproducibility of the MSC from different batches has
been difficult.)   With the increasing amount of adsorption the
adsorbing surface will be progressively covered with more and
more adsorbate molecules so that more than one layer of these
molecules may be formed and a variation in q^{st} values may be
observed with the increasing coverage.   In the present study we
observe that the q^{st} values increase slightly (except for Argon
on 5A) as the surface coverage increases.   The fact that the q^{st}
values are high for N_2 and CH_4 in the low-coverage study of
Chihara   et al. suggests that the adsorbent surface (carbon) and
the adsorbate molecules have higher (absolute value) attraction

potential than that possessed by two like (adsorbate) molecules. Further, the slight increase in values with increasing adsorption in the present high-coverage study indicates that there is some interaction between the adsorbate molecules.

Single Component Diffusion

Mathematical Model

The diffusion of gases in porous solids is generally assumed to follow Fick's second law. This assumption is valid for the diffusion of gases in molecular sieve carbons. The derivation of the partial differential equation to describe the diffusion process in the MSC is based on the following assumptions:

1. The particles of the MSC are isothermal, uniform and spherical.

2. Fickian diffusion may be used to describe the diffusion process within the pores of the MSC.

3. The diffusion coefficient is constant during the adsorption process.

4. At the gas-solid interface, the concentration of the adsorbate is the same as that in the gas phase.

Utilizing the above described assumptions, a mass balance on a spherical particle (27) yields

$$\frac{\partial c}{\partial t} = D \left(\frac{1}{r^2} \right) \frac{\partial}{\partial r} \left(r^2 \frac{\partial c}{\partial r} \right) \tag{7}$$

with
- C = concentration of the adsorbate in the solid
- r = radial position
- t = time
- D = diffusion coefficient

Equation (7) can be solved analytically using the following initial and boundary conditions associated with a constant volume, constant pressure system:

$$\text{At} \quad t = 0 \quad\quad C(0, r) = C_o$$

At $t > 0$

$$\text{at } r = 0 \quad \frac{\partial c(t, 0)}{\partial r} = 0 \tag{8}$$

$$\text{at } r = R \quad C(t, R) = C_\infty$$

where R is the radius of the MSC particle.

In the present study, the amount of gas adsorbed by the MSC was measured experimentally as a function of time. Therefore, it is more useful to calculate the total amount of gas adsorbed at any time by the following relation:

$$M_t = 4\pi \int_0^R (C - C_o) r^2 dr \qquad (9)$$

where M_t = amount adsorbed at any time t.

The solution of Eq. (7) with boundary conditions, Eq.(8), in terms of fractional uptake M_t/M_∞ is given by Crank (28)

$$\frac{M_t}{M_\infty} = 1 - \frac{6}{\pi^2} \sum_{n=1}^{\infty} \frac{1}{n^2} \exp(-n^2\pi^2 tD/r^2) \qquad (10)$$

where D is the diffusivity, M_t is the mass of the sorbate adsorbed in time t, M_∞ is the mass of the sorbate adsorbed at equilibrium, and r is the mean particle diameter.

Comparison of Diffusivity Values

Equation (10) was used to determine the diffusion coefficient of all the gases in both 3A and 5A MSC. The least squares method was used to fit the experimental data with Eq. (10). The diffusion coefficients determined in this manner are shown in Tables 6 and 7 for 3A and 5A MSC respectively. Figures 33, 34, 35, and 36 compare the typical experimental data and the curves computed from Eq. (10) which show, in general, good agreement. The D/r^2 value used for each curve is indicated on the figures. The rates of adsorption of various gases are compared with each other at 0°C, 30°C, and 50°C, respectively, in Figures 33, 34, and 35. The rates for one gas (argon on 3A MSC) are shown at three temperatures in Figure 36.

The diffusivity values range from 10^{-5} for methane at 0°C in 3A MSC to 10^{-2} sec^{-1} for oxygen in 5A MSC at 50°C. Diffusivities in 3A MSC are comparable to those in BF MSC, but lower than in 5A MSC. Among the four gases studied, methane has the lowest diffusional rate and oxygen the highest in all samples. The diffusivity values could be arranged in the following order: CH_4 < N_2 ≈ Ar < O_2. On a relative scale if methane was assigned a diffusivity value of 1, the corresponding values for oxygen, nitrogen and argon at 30°C were about 14, 2, and 2, respectively, in the case of 5A MSC. Similarly, in the case of 3A MSC, the relative diffusivity values at 30°C for methane, oxygen, nitrogen and argon were 1, 160, 8, and 13 respectively. Comparing the rates in 3A and 5A MSC for, say, methane, it was found that the gas diffused in 5A about 15 times as fast as in 3A MSC.

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TABLE 6. DIFFUSIVITY OF GASES IN 3A MSC

Gas	0°C		30°C		50°C	
	P [a] (Torr)	D/r^2 [b] (sec^{-1})	P [a] (Torr)	D/r^2 [b] (sec^{-1})	P [a] (Torr)	D/r^2 [b] (sec^{-1})
N$_2$	73	4.70×10^{-5}	85	2.27×10^{-4}	130	6.71×10^{-4}
	153	5.21×10^{-5}	425	2.67×10^{-4}	290	5.52×10^{-4}
	485	6.92×10^{-5}	780	2.13×10^{-4}	580	8.14×10^{-4}
	907	9.07×10^{-5}	1545	2.19×10^{-4}	1000	7.14×10^{-4}
	1823	1.16×10^{-4}	1990	2.22×10^{-4}	1700	9.14×10^{-4}
	3039	1.59×10^{-4}	3440	2.26×10^{-4}	3500	1.13×10^{-3}
	4025	1.85×10^{-4}	5630	2.32×10^{-4}	5470	1.04×10^{-3}
O$_2$	42	2.07×10^{-3}	577	4.64×10^{-3}	162	5.40×10^{-3}
	138	1.53×10^{-3}	756	5.86×10^{-3}	283	6.12×10^{-3}
	466	2.37×10^{-3}	1197	5.17×10^{-3}	435	1.27×10^{-2}
	680	1.55×10^{-3}	1424	5.02×10^{-3}	630	1.34×10^{-2}
	1143	2.74×10^{-3}	1797	4.10×10^{-3}	857	1.05×10^{-2}
	1513	2.22×10^{-3}	6591	4.14×10^{-3}	1450	5.74×10^{-3}
	2017	1.76×10^{-3}	8466	4.64×10^{-3}	1840	4.79×10^{-3}
CH$_4$	81	8.70×10^{-6}	220	4.23×10^{-5}	210	7.52×10^{-5}
	422	1.35×10^{-5}	430	3.69×10^{-5}	320	6.27×10^{-5}
	717	9.20×10^{-6}	634	2.69×10^{-5}	471	7.64×10^{-5}
	815	1.38×10^{-5}	745	2.61×10^{-5}	690	9.19×10^{-5}
	1192	1.36×10^{-5}	877	3.10×10^{-5}	920	8.47×10^{-5}
	1988	1.18×10^{-5}	1250	4.08×10^{-5}	1045	8.30×10^{-5}
	2583	1.21×10^{-5}	2493	3.72×10^{-5}	1315	9.19×10^{-5}
Ar	227	1.59×10^{-4}	200	3.79×10^{-4}	240	6.33×10^{-4}
	867	1.70×10^{-4}	350	3.43×10^{-4}	1461	4.85×10^{-4}
	877	2.20×10^{-4}	500	3.96×10^{-4}	2130	6.66×10^{-4}
	1196	1.92×10^{-4}	800	3.24×10^{-4}	2935	5.90×10^{-4}
	1512	1.96×10^{-4}	1150	3.62×10^{-4}	3950	5.47×10^{-4}
	2029	1.82×10^{-4}	3020	3.93×10^{-4}	4560	6.05×10^{-4}
	2737	1.95×10^{-4}	6000	3.53×10^{-4}	4980	6.15×10^{-4}

[a] P : Pressure
[b] D/r^2 : Diffusivity

Although the adsorption capacity of MSC for nitrogen and oxygen were approximately the same, there was a large difference in adsorption rates, which means that the adsorbent could be employed in a PSA process depending on a kinetic separation to obtain nitrogen, argon and oxygen from air. By comparing our data on 3A MSC, BF MSC and 5A MSC, it appears that either 3A MSC or BF MSC is better suited in air separation processes because the adsorbent may be predicted to show a higher kinetic selectivity when exposed to a mixture of oxygen and nitrogen. Of the three adsorbents, BF MSC appears to give the best kinetic selectivity for the N$_2$-O$_2$ mixture, with a diffusivity ratio

TABLE 7. DIFFUSIVITY OF GASES IN 5A MSC

Gas	0°C		30°C		50°C	
	P [a] (Torr)	D/r^2 [b] (sec^{-1})	P [a] (Torr)	D/r^2 [b] (sec^{-1})	P [a] (Torr)	D/r^2 [b] (sec^{-1})
N_2	79	5.42×10^{-4}	227	1.88×10^{-3}	56	3.62×10^{-3}
	143	4.72×10^{-4}	1690	1.36×10^{-3}	132	3.06×10^{-3}
	508	2.27×10^{-4}	2129	1.11×10^{-3}	594	4.48×10^{-3}
	665	3.00×10^{-4}	2483	7.04×10^{-4}	1055	5.21×10^{-3}
	924	5.90×10^{-4}	2995	1.19×10^{-3}	1438	2.05×10^{-3}
	2624	3.41×10^{-4}	4112	9.59×10^{-4}	2288	3.44×10^{-3}
	3631	4.80×10^{-4}	5330	8.31×10^{-4}	4181	2.60×10^{-3}
O_2	378	1.86×10^{-3}	67	7.23×10^{-3}	101	8.97×10^{-3}
	602	1.22×10^{-3}	505	4.56×10^{-3}	203	1.44×10^{-2}
	1066	1.38×10^{-3}	1022	5.78×10^{-3}	347	1.09×10^{-2}
	1621	1.30×10^{-3}	1235	7.08×10^{-3}	920	1.58×10^{-2}
	2509	1.49×10^{-3}	1917	6.35×10^{-3}	1157	1.10×10^{-2}
	3019	1.15×10^{-3}	2822	6.89×10^{-3}	1358	1.00×10^{-2}
	3598	1.04×10^{-3}	4866	7.59×10^{-3}	2505	1.07×10^{-2}
CH_4	106	1.95×10^{-4}	970	9.38×10^{-4}	146	1.22×10^{-3}
	157	3.65×10^{-4}	1520	7.66×10^{-4}	223	1.39×10^{-3}
	444	2.67×10^{-4}	2383	3.00×10^{-4}	1225	9.37×10^{-3}
	695	2.14×10^{-4}	2682	2.62×10^{-4}	2037	1.44×10^{-3}
	1009	1.88×10^{-4}	2928	2.76×10^{-4}	2805	1.14×10^{-3}
	1932	2.34×10^{-4}	3402	4.41×10^{-4}	3343	1.21×10^{-3}
	3822	1.97×10^{-4}	3922	4.22×10^{-4}	55	8.93×10^{-4}
Ar	225	5.42×10^{-4}	103	9.43×10^{-4}	145	2.17×10^{-3}
	810	3.34×10^{-4}	174	6.71×10^{-4}	407	2.26×10^{-3}
	970	7.59×10^{-4}	312	1.16×10^{-3}	610	1.77×10^{-3}
	1342	7.69×10^{-4}	1210	1.23×10^{-3}	1533	1.98×10^{-3}
	1496	6.04×10^{-4}	2147	7.85×10^{-4}	3178	2.34×10^{-3}
	2994	4.39×10^{-4}	2586	1.11×10^{-3}	3570	1.63×10^{-3}
	4004	3.29×10^{-4}	3661	8.76×10^{-4}	36˙3	1.82×10^{-3}

[a] P : Pressure
[b] D/r^2 : Diffusivity

(N_2/O_2) of 0.04. Ruthven et al. (24) reported diffusivity values
of 1.2×10^{-4} and 37×10^{-4} sec^{-1} for nitrogen and oxygen on the BF
MSC, respectively, yielding a diffusivity ratio of 0.03. In our
study, high kinetic selectivities are also observed for Ar-O_2 and
CH_4-O_2 on 3A and BF MSC. Studies involving mixture adsorption
are needed to confirm these results.
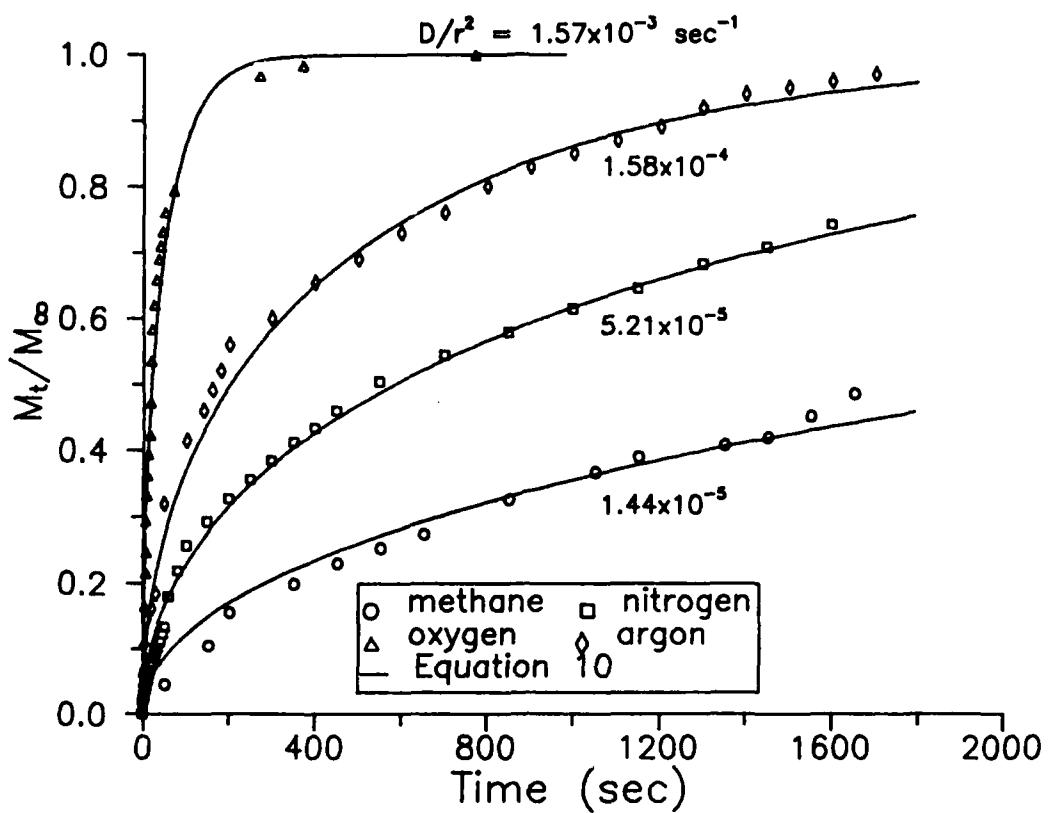
Figure 33. Uptake curves of gases on 3A MSC at 0°C.
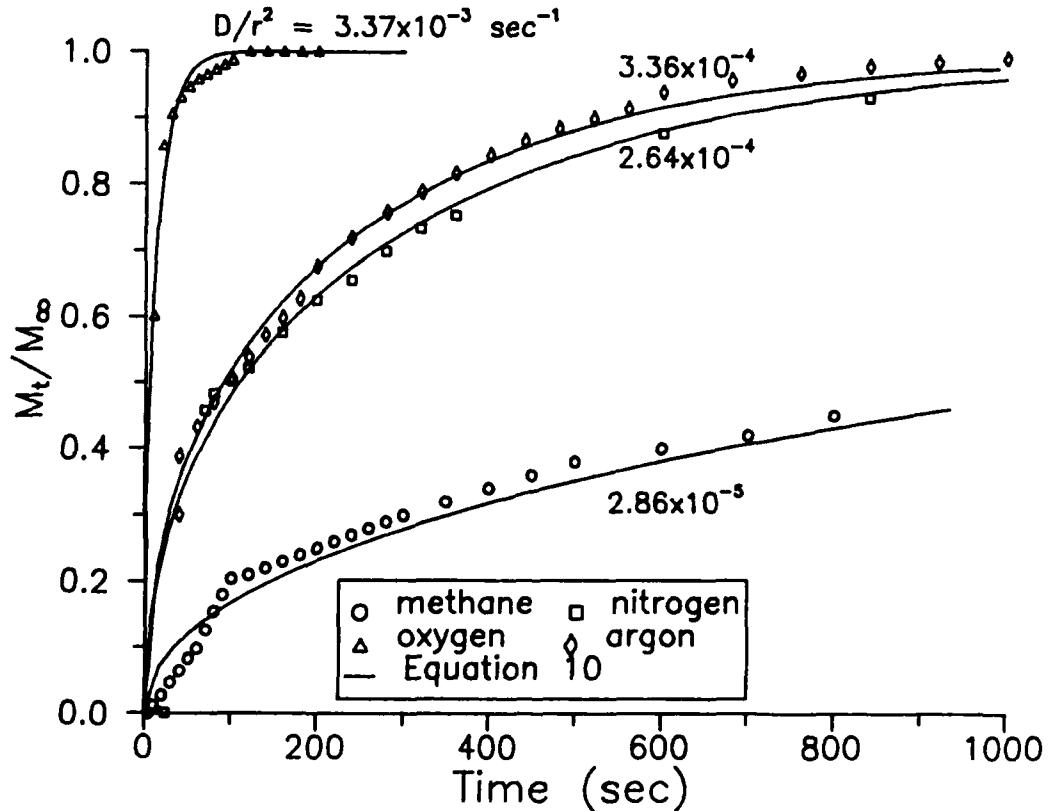
Figure 34. Uptake curves of gases on 3A MSC at 30°C.
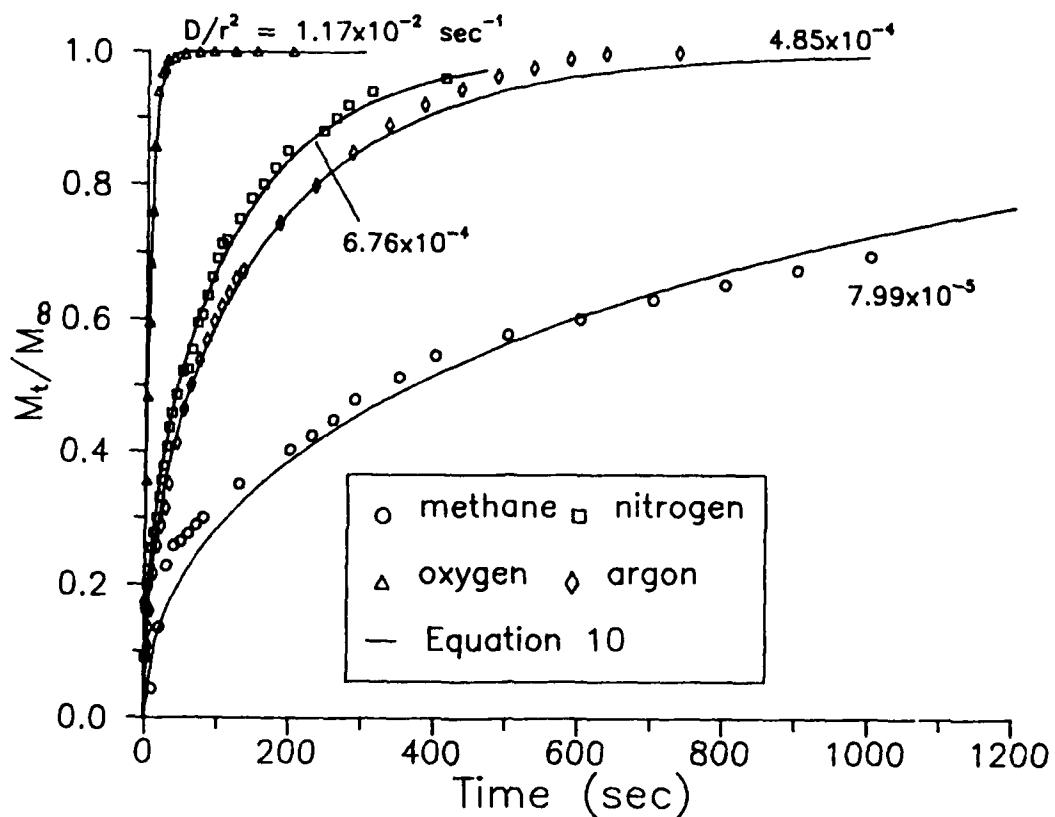
Figure 35. Uptake curves of gases on 3A MSC at 50°C.
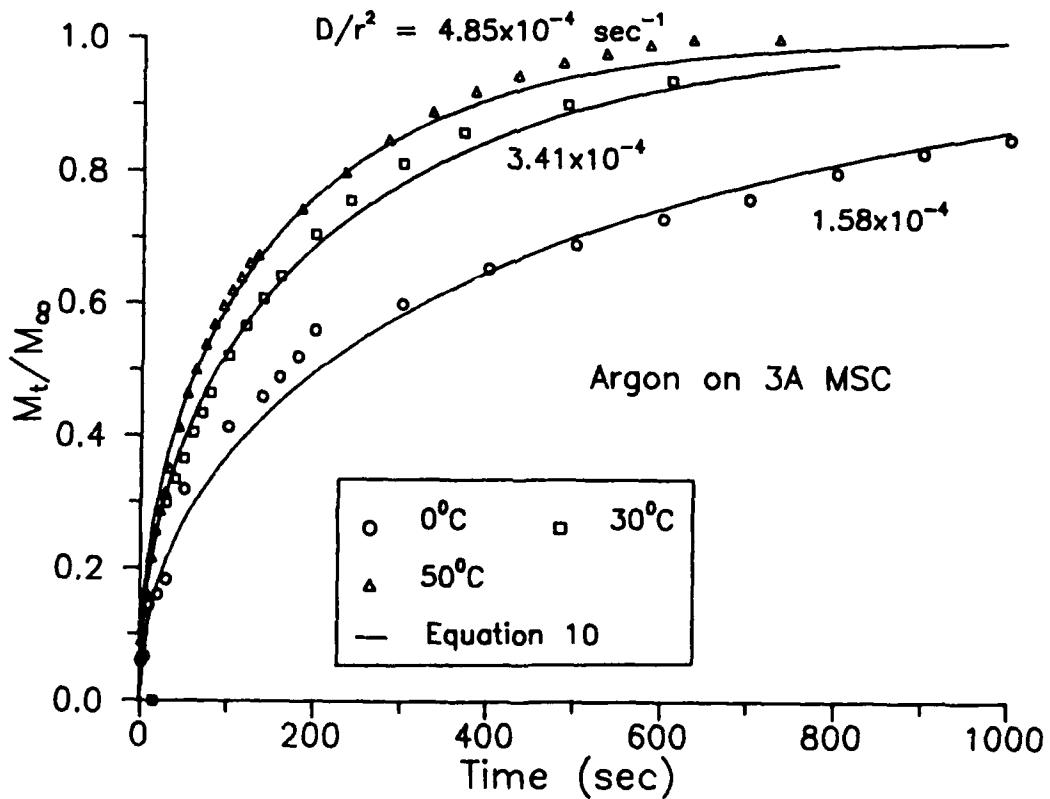
Figure 36. Uptake curves at different temperatures.

Variation of Diffusivity with Temperature and Pressure

The diffusivity values increased with the increasing adsorption temperature, as was expected. Generally speaking, the data obtained in the present study showed that the rate of increase in the diffusivity values was steepest for nitrogen in 3A MSC, and for oxygen in 5A MSC. The values for argon showed a comparatively smaller increase in the diffusivity with increasing temperature. It is interesting to correlate the temperature dependence of the diffusivity (D) using the Arrhenius equation:

$$D = D_0 \exp(-E/|RT|) \qquad (11)$$

where D_0 is the pre-exponential factor, E is the activation energy for diffusion, R is the gas constant, and T is the temperature (Kelvin). From Eq. (11) it is clear that a plot of ln(D) versus (1/T) will be a straight line. Such plots were constructed from the data for each gas on both 3A and 5A MSC. The activation energies for the adsorption were obtained from the slopes of these plots. The average values are listed in Table 8.

TABLE 8. ACTIVATION ENERGY OF DIFFUSION IN 5A AND 3A MSC

	E (KJ/mol)			
	N_2	O_2	CH_4	Ar
5A MSC	27.7	32.2	22.3	18.6
3A MSC	29.2	20.6	27.8	16.6

The activation energy values were high, comparable to the values for isosteric heats of adsorption (Tables 4 and 5) confirming that the diffusion in MSC is an activated process (26). For argon and methane these values were about 19 and 22 KJ/mol, respectively. The values for argon and methane obtained previously (26) in the case of 5A MSC from chromatographic measurements and a moment analysis were about 16 and 20 KJ/mol, respectively. For nitrogen the value of 16 KJ/mol was reported in the same study, and the value in the present study was high, about 28 KJ/mol. The values of activation energy for diffusion could not be correlated well with the isosteric heats of adsorption, although it should be mentioned that the ratio E/q_{st} was in the range of 1 to 2 for the gases studied. Perhaps, such a correlation would be more useful if the adsorption experiments were carried out at extremely low coverage (Henry's law region) of the adsorbate upon the sample, as was done in previous chromatographic measurements (26) from which a ratio of 0.9 was obtained. However, adsorption at very low coverages would not have much practical interest.

In general, the obtained diffusivity values showed no dependency on adsorbate pressure (Figures 37 and 38). The only
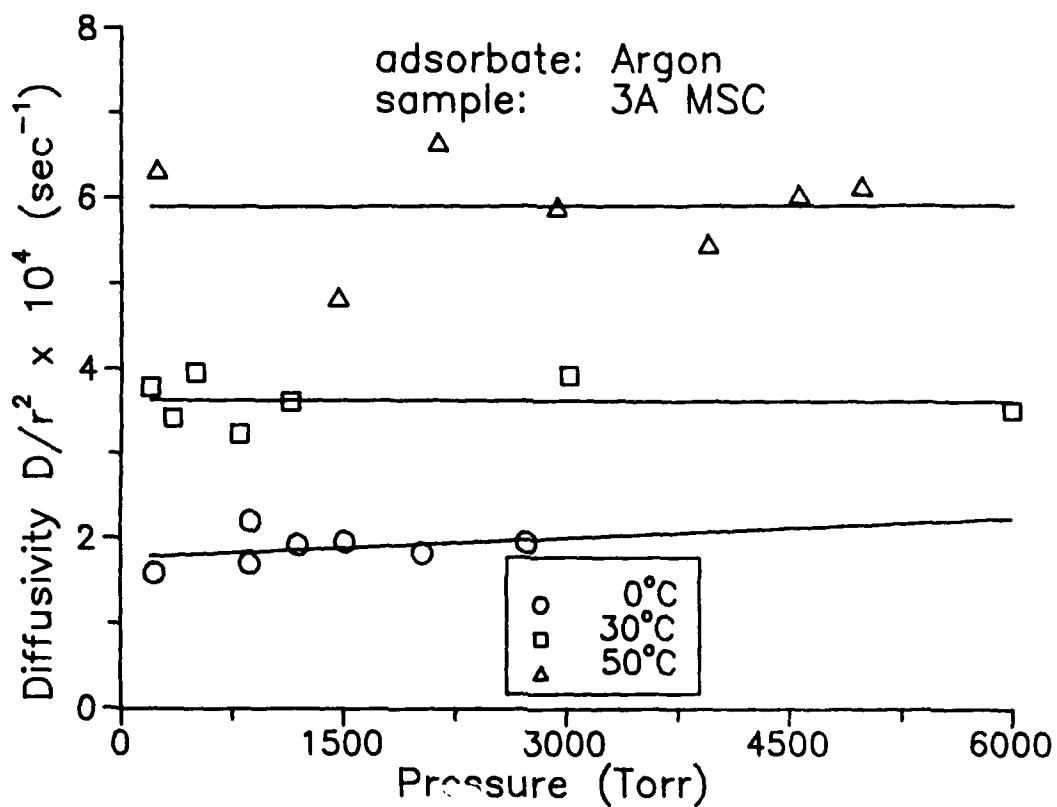
Figure 37. The variation of diffusivity of Ar with pressure.
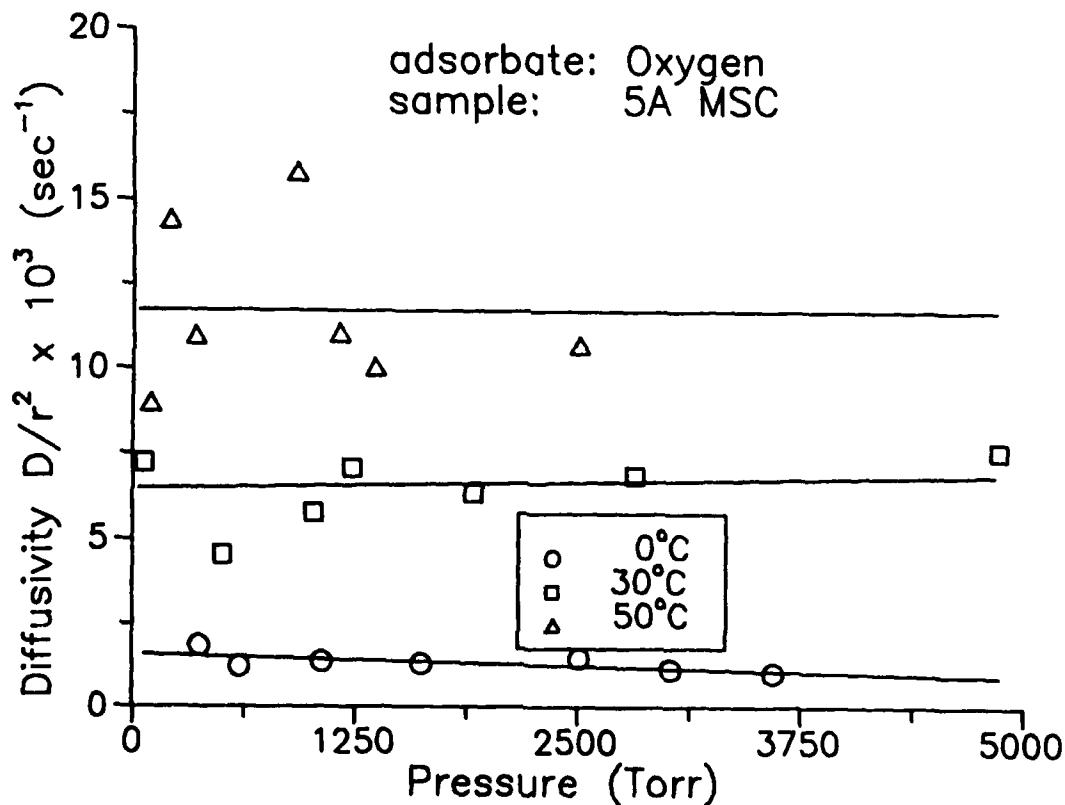
Figure 38. The variation of diffusivity of O_2 with pressure.

dependency observed was in the case of nitrogen adsorbed on 3A
MSC at low temperature (0°C). The diffusivity in this case
appeared to increase with pressure. The independence of
diffusivity with sorbate concentration validates the assumption
of an ideal Fickian model for diffusion. It should be noted that
Kawazoe et al.(29, 30) previously reported the essential
independence of the diffusivity for, as an example, propylene on
5A MSC.

Multicomponent Adsorption

The importance of obtaining information on the adsorption
rate of multicomponent systems can be demonstrated by the
phenomena of competitive adsorption generally observed in
multicomponent systems. The competition for adsorption sites
among interacting adsorbates will not only affect the equilibrium
adsorption capacity of each individual component, but also
influence the diffusion rate of the individual adsorbate.
Furthermore, this competitive adsorption causes the displacement
phenomena commonly observed in rate studies in a multicomponent
system. The result is a maximum in the uptake curve of one of
the species until equilibrium is established due to differences
in diffusion rates and affinity to the adsorbent. The practical
implication of the displacement phenomena is that the displaced
species will break through the adsorption bed and reduce the
effectiveness of the bed.

The apparatus originally designed to carry out the
multicomponent adsorption rate study is described below. The
difficulty associated with this setup for obtaining reliable
multicomponent adsorption rate data is also discussed. Finally,
the new design which will alleviate the difficulties encountered
in the original design is presented.

Original Design of the Multicomponent Adsorption Setup

Due to the low adsorption capacity and fast kinetics
involved in the diffusion of N_2, O_2 and Ar (extremely slow
kinetics for CH_4), a more sensitive way of detecting the
composition change in the gas phase had to be devised.
Therefore, a new well-stirred reactor system was designed and
constructed.

A well-stirred reactor consisting of a 5-liter cylindrical
stainless steel vessel was constructed to study the diffusion and
adsorption of gases in multicomponent systems. Either powder or
pellets could be placed in two equally spaced adjustable baskets
which were attached to the shaft and were rotated at 3300
rev/min. The shaft was driven magnetically by a 1/2 HP motor.
A schematic diagram of the adsorption chamber is shown in Figure
39. The adsorbent could be heated by four heating rods placed
inside stainless steel castings which also served as baffles to

facilitate mixing. The temperature of the system could be controlled to within $\approx 0.5°C$.
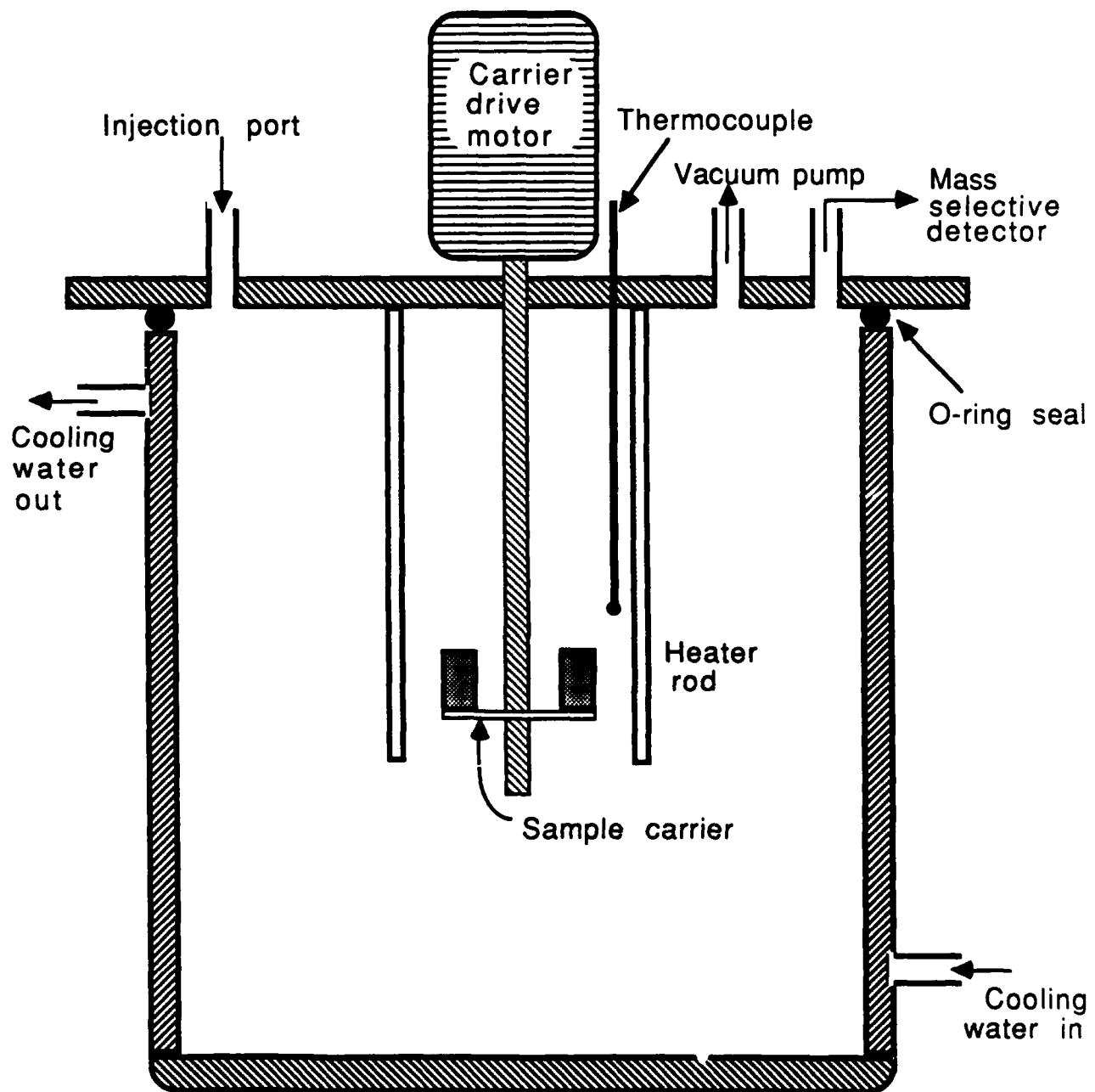
Figure 39. Schematic of the well-stirred reactor.

Adsorption rates were measured by injecting a measured amount of sorbate gases into the adsorption chamber. The amount of each component adsorbed as a function of time could be continuously followed by bleeding a minute quantity of gas from the reactor into a mass selective detector (HP 5970 Series Mass Selective Detector).
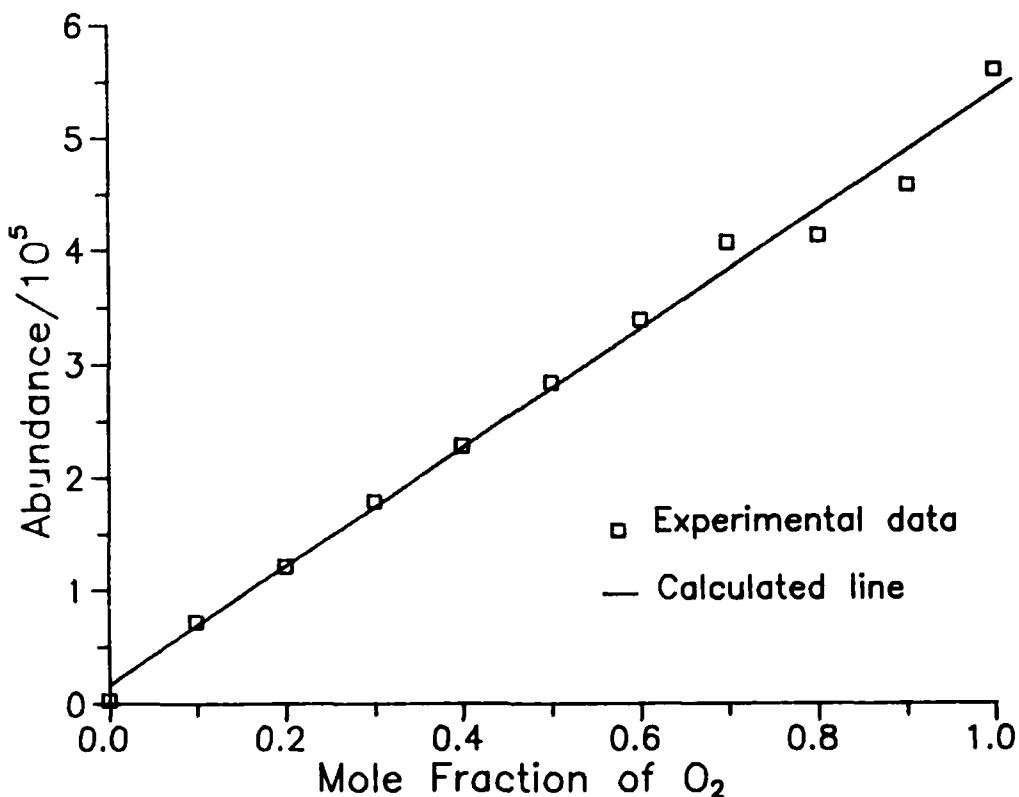
Figure 40. Calibration curve of O_2 in He at 100 Torr.

Difficulty in the Original Design

Since the signal from the mass selective detector is a function of the amount bled into the detector, the signal depends on the gas composition in the reactor as well as on the chamber pressure. Therefore, it is necessary to calibrate the instrument with a known composition under a fixed pressure. A typical calibration curve for O_2 in He at a total pressure of 100 Torr is shown in Figure 40. A good straight line is obtained for the calibration. Calibrations for other gases show similar trends.

The problem arose when the adsorption runs were carried out. The experiments were initiated by activating the sample under vacuum for a fixed period of time. After completing the activation process, a gas mixture was admitted into the reactor creating a sudden surge of chamber pressure which substantially increased the signal from the mass selective detector. The problem is two-fold. First, the sudden increase in the mass spectrometer signal due to the pressure increase made it difficult to determine the initial amount of adsorbate introduced into the system. Second, the subsequent decrease in the MSD signal could be caused by decreased pressure as well as by adsorption. It is essentially impossible to distinguish between these two phenomena due to the sudden surge in initial pressure. After numerous trials, it was decided that a new design would be necessary to obtain accurate, reliable data.

New Design

The purpose of the previous design was to bring a large quantity of gas in contact with the adsorbent and to follow the adsorption process using gas phase composition measurements as a function of time. However, initial pressure changes due to the introduction of the gas interfered with the ability of the MSD to provide signals reflecting the initial gas composition changes. The new design is based on a different concept of bringing together the gas and the adsorbent. After the adsorbent is activated, it is isolated from the gas to be admitted into the chamber. Once the adsorbent is isolated under vacuum, the gas mixture will be admitted to the adsorption chamber. After a steady state is established, the adsorbent is exposed to the gas mixture for the adsorption experiment to eliminate the problem of pressure surge. Thus, the change in the signal from the MSD represents the true composition change in the gas phase. This signal will then be a true measure of the adsorption taking place in the adsorption chamber.

The new design is shown schematically in Figure 41. The main feature of the design is that the sample holder can be isolated from the gas phase by pressing the two plates against the sample holder walls through the two levers. Once the sample is isolated, the gas mixture is released into the chamber. When a steady reading of the signal from the MSD is reached, the adsorbent is exposed to the gas mixture by pulling the two plates away from the sample holder, again through the two levers attached to the chamber. Once the adsorbent is exposed to the gas mixture, the decrease in MSD signals will be continuously recorded. This data will then be used to determine the rate of adsorption and the adsorption equilibrium for a multicomponent system. A photograph of the newly designed multicomponent adsorption system is shown in Figure 42.

IV. CONCLUSIONS

From the results obtained up to date, the following conclusions can be made:

1. It appears that experimental evidence shows that MSC adsorbed relatively small amounts of water when it was exposed to ambient air for an extended period. This phenomenon has been previously stated although experimental data were somewhat scarce.

2. There is no need to activate (heat) the sample after adsorption at low pressures. Desorption under vacuum appears to be sufficient to produce a clean adsorbing surface.

3. Both the Langmuir model and the VSM are used to describe

41
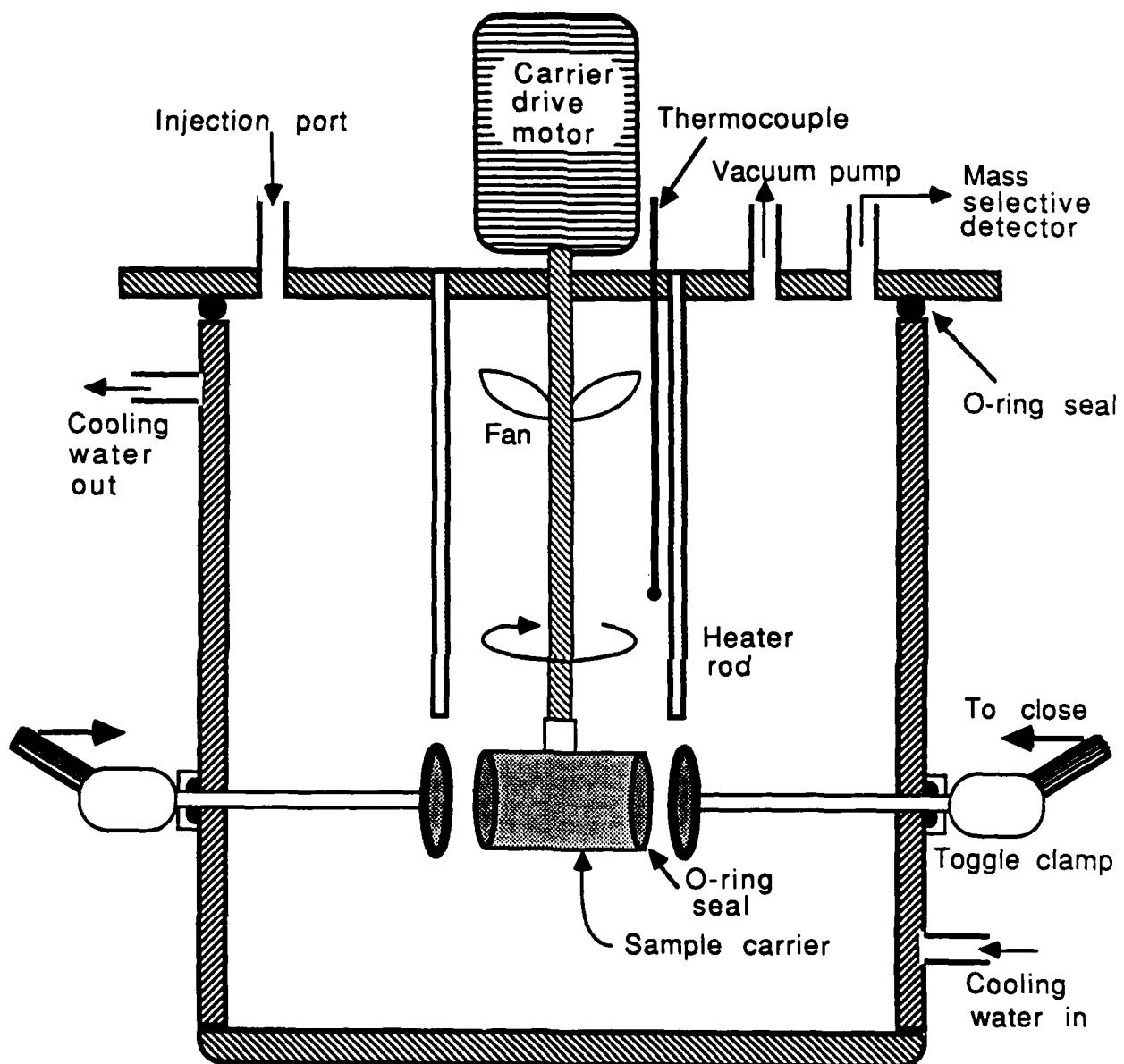
Figure 41. New design for the well-stirred reactor.

the equilibrium adsorption data for the four gases
(methane, oxygen, nitrogen and argon) studied over the range
of adsorbate pressures 0-10,000 Torr. Some deviation is
observed at high pressures for the Langmuir model.

4. The equilibrium adsorption capacities for the four gases
are higher for 5A MSC than for 3A MSC.
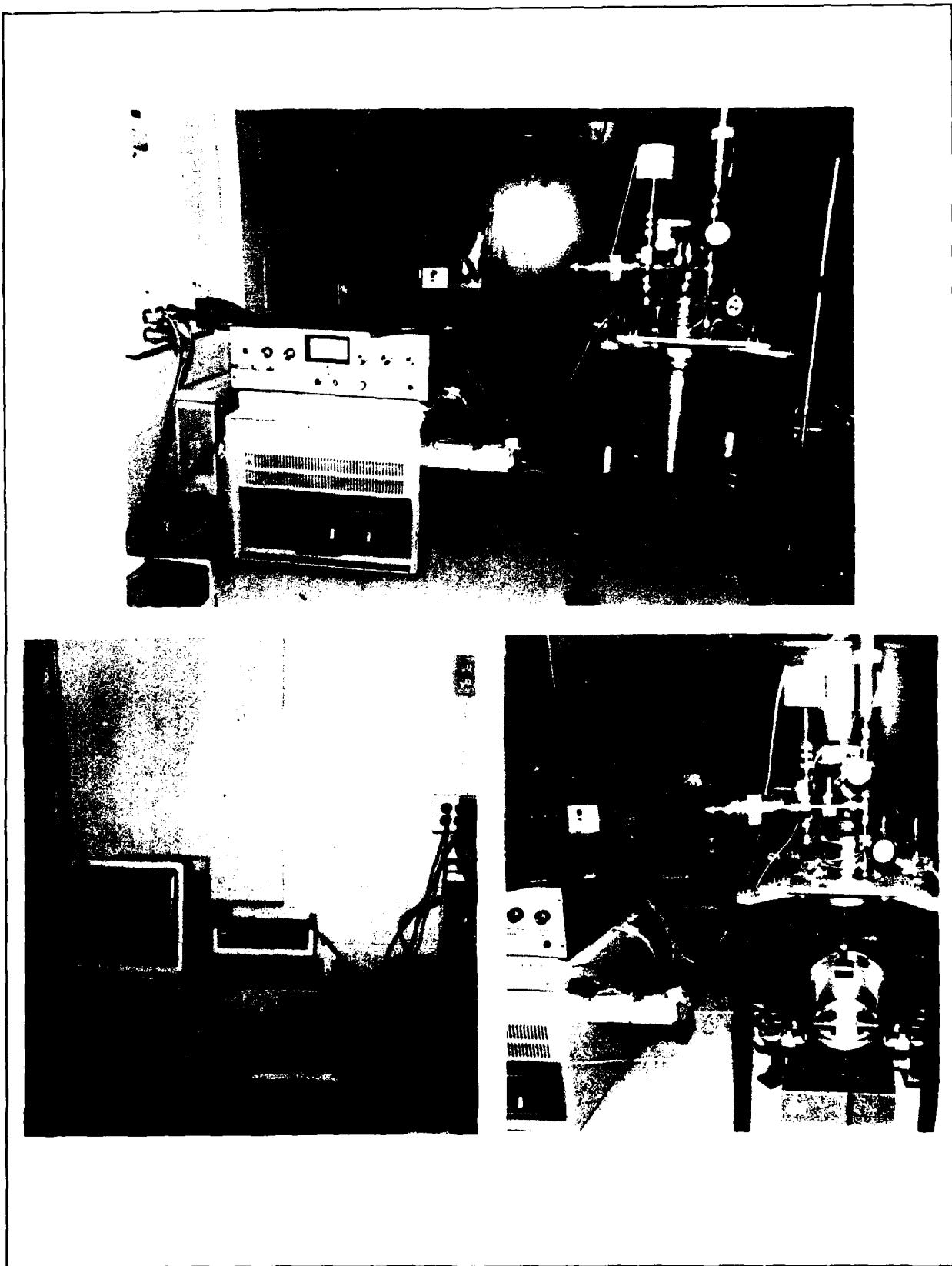
Figure 42.   Photographs of the well-stirred reactor.

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5. The equilibrium adsorption capacities generally show the expected trend with temperature, *viz.*, the capacities decrease with increasing temperature. Only in the case of methane on 3A MSC, is the capacity at 30°C higher than at 0°C at pressures less than 2,500 Torr, probably because equilibrium was not reached due to the extremely slow diffusion rate of methane at this temperature.

6. The adsorption rate of methane is the slowest of the four gases, while that of oxygen is the fastest. Methane adsorption in 3A is considerably slower than in 5A MSC. The adsorption of oxygen in both 5A and 3A occurs at about the same rate. Nitrogen adsorption in 3A is slower than in 5A, thus making 3A a better adsorbent for kinetic separation of air components in a PSA process.

7. The diffusivity values showed no dependency on the pressure. They increased with increasing temperature as expected.

8. The isosteric heats of adsorption appear to increase slightly with an increase in the surface coverage indicating that there is little energetic heterogeneity toward the gases studied. The slight increase in the isosteric heat of adsorption may be due to the interaction among adsorbed molecules.

V. RECOMMENDATIONS FOR FUTURE WORK

The following research activities are recommended.

Measurement of Adsorption and Diffusion of Binary Gases

The new design described in the previous section should be used to obtain data for the adsorption and diffusion of binary gases at 0°C, 30°C, and 50°C and in a pressure range of 0-10,000 Torr. Both the effects of coadsorption of binary gases and the displacement phenomena should be investigated.

Model Prediction for Multicomponent Adsorption from Single Component Adsorption Data

The Langmuir, VSM, IAST, and modified Langmuir-Sips isotherm equations should be used to predict multicomponent adsorption isotherms from single component data. The mixture adsorption isotherms obtained from the model should be compared with those obtained from experimental measurements.

Mathematical Modeling for Multicomponent Diffusion

A mathematical model for multicomponent diffusion should be developed. This model will then be used to describe the diffusional process occurring in the multicomponent diffusion experiments proposed in Section V; the diffusivity obtained from the multicomponent systems will be compared with those obtained from single component systems.

NOMENCLATURE

b = a constant in the Langmuir isotherm equation, 1/Torr
b_{01} = a constant in the VSM equation, mmol/g·Torr
b_1 = Henry's law constant in the VSM equation, mmol/g·Torr
C = adsorbate concentration in the solid, mmol/cc
D = diffusion coefficient, cm^2/sec
D_0 = pre-exponential factor in Eq. (11)
E = activation energy diffusion, KJ/mol
K' = Henry's law constant, mg/g·Torr
m_1 = a constant in the VSM equation, g/mmol
M_t = mass adsorbed at time t, g
M_∞ = mass adsorbed at equilibrium, g
n_{01} = a constant in the VSM equation, mmol/g
n_1 = amount adsorbed, mmol/g
n^∞_1 = limiting amount adsorbed, mmol/g
P = pressure, Torr
q = adsorption capacity, mmol/g
q_1 = isosteric heat of adsorption at infinite dilution, KJ/mol
q_m = monolayer adsorption capacity, mmol/g
q^{st} = isosteric heat of adsorption, KJ/mol
R = gas constant, KJ/mol·°K
r = radial position in the pore, cm; mean particle diameter, cm
R = radius of the MSC particle, cm
r_1 = a constant in the VSM equation, °K
T = temperature, °K
t = time, sec
w = adsorbed amount, mg/g

Greek Symbols

α_{1v} = a parameter describing nonideality in the VSM equation
θ = surface coverage, n_1/n^∞_1

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APPENDIX A

(Adsorption Data)

```
Adsorbent       : 5A MSC
Adsorbate       : none
Adsorption Temp : 26°C
Figure number   :  6
Notes     : Weight loss

P (Torr)           Wt. %
   750.0        100.000
   725.0         99.884
   700.0         99.780
   673.0         99.734
   650.0         99.699
   625.0         99.664
   600.0         99.618
   572.0         99.572
   543.0         99.525
   513.0         99.468
   470.0         99.410
   406.0         99.317
   351.0         99.236
   301.0         99.155
   248.0         99.051
   198.0         98.935
   146.0         98.808
    99.0         98.727
    48.0         98.646
    20.1         98.588
    14.0         98.576
    10.0         98.565
     5.0         98.553
     2.0         98.542
     0.3         98.530
     0.0         98.513
```

```
Adsorbent       : 3A MSC
Adsorbate       : none
Adsorption Temp : 26°C
Figure number   :  6
Notes     : Weight loss

P (Torr)           Wt. %
   750.0        100.000
   718.0         99.997
   660.0         99.985
   595.2         99.953
   475.4         99.819
   357.7         99.658
   233.6         99.511
   148.9         99.386
    46.7         99.228
    18.8         99.180
     3.8         99.142
     0.8         99.124
     0.0         99.086
```

```
Adsorbent       : 5A MSC
Adsorbate       : Oxygen
Adsorption Temp : 30°C
Figure number   :  7
Notes     : Activation

P (Torr)          q (mmol/g)
    0.0            0.0000
   13.2            0.0051
   49.4            0.0253
  106.9            0.0532
  132.7            0.0653
  187.4            0.0903
  269.4            0.1274
  365.8            0.1693
  388.6            0.1792
  476.0            0.2162
  596.4            0.2662
  636.0            0.2863
  663.1            0.2966
  706.2            0.3212
```

```
Adsorbent       : 5A MSC
Adsorbate       : Oxygen
Adsorption Temp : 30°C
Figure number   :  7
Notes   :   Desorption/ activ.

P (Torr)          q (mmol/g)
   670.3           0.3133
   604.9           0.2880
   559.6           0.2715
   495.6           0.2443
   405.4           0.2106
   295.6           0.1611
   192.1           0.1115
    98.5           0.0671
    22.7           0.0301
     0.0           0.0211
```

```
Adsorbent        : 5A MSC          Adsorbent        : 5A MSC
Adsorbate        : Oxygen          Adsorbate        : Oxygen
Adsorption Temp : 30°C             Adsorption Temp : 30°C
Figure number   : 7               Figure number   : 8
Notes        : No activation      Notes        : 13-49 Torr

   P (Torr)      q (mmol/g)         Time (sec)           Mt/M∞
      0.0         0.0000                6              0.3191
     12.2         0.0037               10              0.3838
     49.8         0.0231               20              0.4894
     87.7         0.0422               30              0.6117
    214.6         0.1068               40              0.7021
    361.0         0.1674               50              0.7766
    510.3         0.2294               60              0.8245
    539.8         0.2419               80              0.8883
    666.3         0.2944              100              0.9255
                                      120              0.9415


Adsorbent        : 5A MSC          Adsorbent        : 5A MSC
Adsorbate        : Oxygen          Adsorbate        : Oxygen
Adsorption Temp : 30°C             Adsorption Temp : 30°C
Figure number   : 8               Figure number   : 8
Notes        : 49-107 Torr        Notes        : 366-389 Torr

   Time (sec)       Mt/M∞           Time (sec)           Mt/M∞
       2           0.1139                6              0.5833
      10           0.5125               10              0.7500
      18           0.7900               16              0.8438
      28           0.9039               20              0.8750
      40           0.9359               30              0.9167
      50           0.9466               40              0.9375
      60           0.9537               60              0.9479
      70           0.9573
      80           0.9609


Adsorbent        : 5A MSC          Adsorbent        : 5A MSC
Adsorbate        : Oxygen          Adsorbate        : Oxygen
Adsorption Temp : 30°C             Adsorption Temp : 30°C
Figure number   : 8               Figure number   : 8
Notes        : 510-540 Torr       Notes        : 636-663 Torr

   Time (sec)       Mt/M∞           Time (sec)           Mt/M∞
       4           0.4286                4              0.3725
      10           0.5714               10              0.8235
      20           0.6349               20              0.8824
      30           0.6825               30              0.9118
      40           0.7381               40              0.9314
      50           0.7698               50              0.9412
      60           0.7937               60              0.9608
      80           0.8492               80              0.9804
     120           0.9048
     140           0.9206
```

Adsorbent	: 5A MSC
Adsorbate	: Oxygen
Adsorption Temp	: 30°C
Figure number	: 9
Notes	: 915-1018

Time (sec)	Mt/M_∞
2.0	0.0862
4.0	0.1385
8.0	0.2864
16.0	0.4953
30.0	0.6693
60.0	0.7389
120.0	0.7737
240.0	0.8260
480.0	0.9217
880.0	0.9800

Adsorbent	: 5A MSC
Adsorbate	: Oxygen
Adsorption Temp	: 30°C
Figure number	: 9
Notes	: 2569-2673 Torr

Time (sec)	Mt/M_∞
2.0	0.1328
4.0	0.1756
8.0	0.2506
16.0	0.4219
30.0	0.6574
60.0	0.8109
100.0	0.9072
140.0	0.9643
170.0	0.9929

Adsorbent	: 5A MSC
Adsorbate	:Oxygen
Adsorption Temp	: 30°C
Figure number	: 10
Notes	: 1st run at high-pressure

P (Torr)	q (mmol/g)
812	0.3308
915	0.3685
1081	0.4430
1380	0.5442
1794	0.6484
2311	0.7844
2828	0.9028
3345	0.9979
3862	1.0929

Adsorbent	: 5A MSC
Adsorbate	: Oxygen
Adsorption Temp	: 30°C
Figure number	: 9
Notes	: 1432-1535 Torr

Time (sec)	Mt/M_∞
4.0	0.0008
8.0	0.1266
16.0	0.3648
30.0	0.5765
60.0	0.6625
120.0	0.7287
240.0	0.8147
480.0	0.9074
680.0	0.9868

Adsorbent	: 5A MSC
Adsorbate	: Oxygen
Adsorption Temp	: 30°C
Figure number	: 9
Notes	3215-3345 Torr

Time (sec)	Mt/M_∞
2.0	0.2454
4.0	0.2779
8.0	0.3223
16.0	0.4318
30.0	0.5916
60.0	0.7810
100.0	0.8994
140.0	0.9349
180.0	0.9763
190.0	0.9941

Adsorbent	: 5A MSC
Adsorbate	: Oxygen
Adsorption Temp	: 30°C
Figure number	: 10
Notes	: 2nd run at high pressure

P (Torr)	q (mmol/g)
812	0.3483
915	0.3860
1019	0.4296
1432	0.5630
1536	0.5949
2053	0.7426
2570	0.8552
2673	0.8812
3216	1.0003
3345	1.0153
3862	1.0986

Adsorbent	: 5A MSC
Adsorbate	: Oxygen
Adsorption Temp	: 30°C
Figure number	: 10
Notes	: 3rd run at low-pressure

P (Torr)	q (mmol/g)
13	0.0055
49	0.0255
107	0.0534
133	0.0654
187	0.0903
269	0.1272
366	0.1693
389	0.1791
476	0.2162
596	0.2662
636	0.2863

Adsorbent	: 5A MSC
Adsorbate	: Oxygen
Adsorption Temp	: 30°C
Figure number	: 10
Notes	: 4th run at low-pressure

P (Torr)	q (mmol/g)
12	0.0040
50	0.0233
88	0.0422
215	0.1067
361	0.1672
510	0.2293
540	0.2418
666	0.2942

Adsorbent	: 3A MSC
Adsorbate	: Oxygen
Adsorption Temp	: 30°C
Figure number	: 11
Notes	: 1st run experimental data

P (Torr)	q (mmol/g)
812	0.3856
915	0.4301
1019	0.4579
1432	0.5859
1536	0.6137
2053	0.7610
2518	0.8483
3087	0.9676
3190	0.9828
3862	1.0964

Adsorbent	: 3A MSC
Adsorbate	: Oxygen
Adsorption Temp	: 30°C
Figure number	: 11
Notes	: 2nd run experimental data

P (Torr)	q (mmol/g)
17	0.0798
25	0.0842
66	0.0936
130	0.1202
186	0.1467
252	0.1818
332	0.2089
432	0.2448
577	0.3070
756	0.3867
967	0.4714
1197	0.5274
1424	0.5958
1797	0.6971
2213	0.7954
2575	0.8714
2893	0.9337
3220	0.9921
3536	1.0503
3973	1.1031
4513	1.1836
5046	1.2473
5590	1.3112
6164	1.3750
6591	1.4200

Adsorbent	: 5A MSC
Adsorbate	: Oxygen
Adsorption Temp	: 0°C
Figure number	: 12
Notes	: 1st run

P (Torr)	q (mmol/g)
16	0.0889
110	0.1820
184	0.2679
275	0.3587
378	0.4410
495	0.5125
698	0.6415
1066	0.8389
1455	1.0103
1892	1.1297
2509	1.3224
3019	1.4592
3598	1.6000
4180	1.7143

Adsorbent	: 5A MSC
Adsorbate	: Oxygen
Adsorption Temp	: 0°C
Figure number	: 12
Notes	: 2nd run

P (Torr)	q (mmol/g)
17	0.0823
72	0.1390
142	0.2094
225	0.2823
340	0.3781
503	0.4884
602	0.5573
737	0.6316
862	0.6989
1147	0.8433
1294	0.9134
1621	1.0677
2065	1.1918
2485	1.3241
2638	1.3679
3105	1.4992
3706	1.6383
4230	1.7445

Adsorbent	: 5A MSC
Adsorbate	: Oxygen
Adsorption Temp	: 30°C
Figure number	: 12
Notes	: 1st run

P (Torr)	q (mmol/g)
812	0.2934
915	0.3316
1070	0.3711
1277	0.4653
1525	0.5250
1949	0.6662
2352	0.7654
2818	0.8662
3345	0.9982
3862	1.1062

Adsorbent	: 5A MSC
Adsorbate	: Oxygen
Adsorption Temp	: 30°C
Figure number	: 12
Notes	: 2nd run

P (Torr)	q (mmol/g)
812	0.3308
915	0.3685
1081	0.4430
1380	0.5442
1794	0.6484
2311	0.7844
2828	0.9028
3345	0.9979
3862	1.0929

Adsorbent	: 5A MSC		Adsorbent	: 5A MSC
Adsorbate	: Oxygen		Adsorbate	: Oxygen
Adsorption Temp	: 30°C		Adsorption Temp	: 30°C
Figure number	: 12		Figure number	: 12
Notes	: 3st run		Notes	: 4nd run

P (Torr)	q (mmol/g)		P (Torr)	q (mmol/g)
812	0.3483		13	0.0055
915	0.3860		49	0.0255
1019	0.4296		107	0.0534
1432	0.5630		133	0.0654
1536	0.5949		187	0.0903
2053	0.7426		269	0.1272
2570	0.8552		366	0.1693
2673	0.8812		389	0.1791
3216	1.0003		476	0.2162
3345	1.0153		596	0.2662
3862	1.0986		636	0.2863

Adsorbent	: 5A MSC		Adsorbent	: 5A MSC
Adsorbate	: Oxygen		Adsorbate	: Oxygen
Adsorption Temp	: 30°C		Adsorption Temp	: 50°C
Figure number	: 12		Figure number	: 12
Notes	: 5th run		Notes	: 1st run

P (Torr)	q (mmol/g)		P (Torr)	q (mmol/g)
12	0.0040		22	0.0757
50	0.0233		71	0.0925
88	0.0422		178	0.1284
215	0.1067		387	0.1911
361	0.1672		641	0.2617
510	0.2293		977	0.3432
540	0.2418		1358	0.4413
666	0.2942		1670	0.5090
			2040	0.5957
			2505	0.6982

Adsorbent	: 5A MSC		2991	0.7857
Adsorbate	: Oxygen		3545	0.8749
Adsorption Temp	: 50°C		4173	0.9749
Figure number	: 12			
Notes	: 2nd run			

P (Torr)	q (mmol/g)
22	0.0892
101	0.1156
203	0.1447
347	0.1838
617	0.2527
691	0.2701
920	0.2959
1157	0.3395
1392	0.4208
1754	0.5098
2335	0.6242
2615	0.6800
3201	0.7747
4165	0.9276

Adsorbent	: 3A MSC
Adsorbate	: Oxygen
Adsorption Temp	: 0°C
Figure number	: 13
Notes	:

P (Torr)	q (mmol/g)
13	0.0913
42	0.2058
123	0.3963
268	0.4455
466	0.5675
680	0.7224
870	0.8929
1143	1.0201
1513	1.1659
2017	1.2892
2786	1.4711
3484	1.6026
4504	1.8266

Adsorbent	: 3A MSC
Adsorbate	: Oxygen
Adsorption Temp	: 0°C
Figure number	: 13
Notes	:

P (Torr)	q (mmol/g)
5	0.0684
45	0.1084
122	0.3444
226	0.4413
365	0.5781
563	0.7781
767	0.8743
1025	1.0076
1368	1.1626
1732	1.2693
2296	1.4494
2956	1.6579
3737	1.7785
4653	1.9025

Adsorbent	: 3A MSC
Adsorbate	: Oxygen
Adsorption Temp	: 30°C
Figure number	: 13
Notes	:

P (Torr)	q (mmol/g)
812	0.3856
915	0.4301
1019	0.4579
1432	0.5859
1536	0.6137
2053	0.7610
2518	0.8483
3087	0.9676
3190	0.9828
3862	1.0964

Adsorbent	: 3A MSC
Adsorbate	: Oxygen
Adsorption Temp	: 30°C
Figure number	: 13
Notes	:

P (Torr)	q (mmol/g)
17	0.0798
25	0.0842
66	0.0936
130	0.1202
186	0.1467
252	0.1818
332	0.2089
432	0.2448
577	0.3070
756	0.3867
967	0.4714
1197	0.5274
1424	0.5958
1797	0.6971
2213	0.7954
2575	0.8714
2893	0.9337
3220	0.9921
3536	1.0503
3973	1.1031
4513	1.1836
5046	1.2473
5590	1.3112

Adsorbent   : 3A MSC
Adsorbate   : Oxygen
Adsorption Temp : 50°C
Figure number   : 13
Notes   : 1st run

P (Torr)	q (mmol/g)
5	0.1631
14	0.1675
46	0.1725
110	0.1825
162	0.1922
283	0.2245
435	0.2534
630	0.2960
857	0.3602
1140	0.4384
1450	0.4923
1840	0.5815
2378	0.6871
2875	0.7749
3400	0.8426
4240	0.9349
4790	1.0157

Adsorbent   : 5A MSC
Adsorbate   : Methane
Adsorption Temp : 30°C
Figure number   : 14
Notes   : No activation

P (torr)	q (mmol/g)
0.0	0.0000
7.2	0.0200
21.2	0.0741
49.1	0.1548
100.0	0.2809
165.2	0.4108
252.4	0.5524
354.4	0.6881
488.2	0.8553
656.4	1.0175
692.5	1.0498

Adsorbent   : 3A MSC
Adsorbate   : Oxygen
Adsorption Temp : 50°C
Figure number   : 13
Notes   : 2nd run

P (Torr)	q (mmol/g)
10	0.0781
79	0.0961
237	0.1617
389	0.2077
695	0.2868
995	0.3495
1510	0.4793
2033	0.5866
2739	0.7213
4165	0.9390

Adsorbent   : 5A MSC
Adsorbate   : Methane
Adsorption Temp : 30°C
Figure number   : 14
Notes   : Activation

P (torr)	q (mmol/g)
12.8	0.0407
79.6	0.2258
151.7	0.3648
284.5	0.5868
304.7	0.6233
398.2	0.7475
532.8	0.9005
563.9	0.9350
672.5	1.0255

Adsorbent   : 5A MSC
Adsorbate   : Methane
Adsorption Temp : 30°C
Figure number   : 14
Notes   : Desorption data

P (torr)	q (mmol/g)
604.4	0.9815
426.0	0.8143
294.0	0.6301
148.0	0.3991
17.3	0.0924

```
Adsorbent        : 3A MSC
Adsorbate        : Methane
Adsorption Temp  : 30°C
Figure number    : 15
Notes            : 1st run
```

P (Torr)	q (mmol/g)
812	1.4083
915	1.4783
1070	1.5663
1380	1.7592
1794	1.9547
2311	2.0856
2828	2.1660
3345	2.2716

```
Adsorbent        : 3A MSC
Adsorbate        : Methane
Adsorption Temp  : 30°C
Figure number    : 15
Notes            : Desorption data
```

P (Torr)	q (mmol/g)
0	0.4361
1	0.5337
16	0.5797
108	0.7902
172	0.9351
275	0.9897
473	1.0729
747	1.2165
1077	1.4592
1393	1.6169
1916	1.9555
2431	2.1313
2929	2.3066
3473	2.3985
4008	2.5357

```
Adsorbent        : 3A MSC
Adsorbate        : Methane
Adsorption Temp  : 30°C
Figure number    : 15
Notes            : 2nd run
```

P (Torr)	q (mmol/g)
18	0.2340
28	0.2510
82	0.3191
123	0.3618
161	0.5964
220	0.6646
280	0.7329
360	0.9268
430	1.0370
525	1.1812
634	1.3258
745	1.4371
877	1.5655
985	1.6934
1250	1.8086
1675	1.9111
1930	2.0010
2493	2.0820

Adsorbent	: 5A MSC
Adsorbate	: Methane
Adsorption Temp	: 30°C
Figure number	: 16
Notes	: 1st run at high-pressure

P (Torr)	q (mmol/g)
812	0.9480
915	1.0183
1070	1.1587
1381	1.2640
1794	1.4630
2311	1.6269
2829	1.7439
3346	1.8844
3863	1.9546

Adsorbent	: 5A MSC
Adsorbate	: Methane
Adsorption Temp	: 30°C
Figure number	: 16
Notes	: 2nd run at high-pressure

P (Torr)	q (mmol/g)
812	0.9680
915	1.0410
1070	1.1850
1380	1.2990
1749	1.5080
2311	1.6850
2828	1.8150
3345	1.9690
3862	2.0520

Adsorbent	: 5A MSC
Adsorbate	: Methane
Adsorption Temp	: 30°C
Figure number	: 16
Notes	: 3rd run at low-pressure

P (Torr)	q (mmol/g)
7	0.0198
21	0.0741
49	0.1548
100	0.2809
165	0.4108
252	0.5524
354	0.6881
488	0.8553

Adsorbent	: 5A MSC
Adsorbate	: Methane
Adsorption Temp	: 30°C
Figure number	: 16
Notes	: 4th run at low-pressure

P (Torr)	q (mmol/g)
13	0.0407
80	0.2258
152	0.3648
285	0.5868
305	0.6233
398	0.7475
533	0.9005

Adsorbent	: 3A MSC
Adsorbate	: Methane
Adsorption Temp	: 30°C
Figure number	: 17
Notes	: 1st run at high-pressure

P (Torr)	q (mmol/g)
812	1.044
915	1.097
1019	1.142
1432	1.379
1536	1.407
1949	1.526
2285	1.635
2828	1.884
3190	1.919
3862	2.011

Adsorbent	: 3A MSC
Adsorbate	: Methane
Adsorption Temp	: 30°C
Figure number	: 17
Notes	: 2nd run at high pressure

P (Torr)	q (mmol/g)
822	1.249
915	1.294
1019	1.347
1380	1.549
1701	1.616
2311	1.792
2828	1.923
3345	2.003
3862	2.084

```
Adsorbent         : 3A MSC          Adsorbent         : 3A MSC
Adsorbate         : Methane         Adsorbate         : Methane
Adsorption Temp   : 30°C            Adsorption Temp   : 30°C
Figure number     : 17             Figure number     : 17
Notes        : 3rd run at          Notes        : 4th run at
             low-pressure                       low-pressure

   P (Torr)       q (mmol/g)           P (Torr)       q (mmol/g)
       44           0.410                 10           0.342
      530           0.774                 25           0.384
      590           0.808                 90           0.453
      690           0.869                130           0.454
      876           1.000                210           0.464
                                         320           0.542
                                         471           0.621
                                         648           0.792


Adsorbent         : 5A MSC          Adsorbent         : 5A MSC
Adsorbate         : Methane         Adsorbate         : Methane
Adsorption Temp   : 0°C             Adsorption Temp   : 30°C
Figure number     : 18             Figure number     : 18
Notes             :                Notes        : 1st run at
                                                low pressure

   P (Torr)       q (mmol/g)           P (Torr)       q (mmol/g)
       14           0.2128                13           0.0407
       52           0.4262                80           0.2258
       93           0.5954               152           0.3648
      150           0.7739               285           0.5868
      205           0.9080               305           0.6233
      272           1.0381               398           0.7475
      359           1.1908               533           0.9005
      459           1.3305               564           0.9350
      586           1.5063               673           1.0255
      715           1.6645
      920           1.8954        Adsorbent         : 5A MSC
     1153           2.0916        Adsorbate         : Methane
     1614           2.2892        Adsorption Temp   : 30°C
     2323           2.5196        Figure number     : 18
     3145           2.7175           Notes      : 3rd run at
                                                high pressure

                                     P (Torr)       q (mmol/g)
                                        812           0.9680
                                        915           1.0410
                                       1070           1.1850
                                       1380           1.2990
                                       1749           1.5080
                                       2311           1.6850
                                       2828           1.8150
                                       3345           1.9690
                                       3862           2.0520
```

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```
Adsorbent       : 5A MSC          Adsorbent       : 5A MSC
Adsorbate       : Methane         Adsorbate       : Methane
Adsorption Temp : 30°C            Adsorption Temp : 50°C
Figure number   : 18             Figure number   : 18
Notes       : 2nd run at          Notes       :
              high pressure
                                    P (Torr)      q (mmol/g)
   P (Torr)      q (mmol/g)            13           0.1422
        7          0.0198              76           0.2191
       21          0.0741             159           0.3187
       49          0.1548             275           0.4324
      100          0.2809             454           0.5832
      165          0.4108             651           0.7212
      252          0.5524             908           0.8740
      354          0.6881            1571           1.1655
      488          0.8553            2262           1.4268
      656          1.0175            3223           1.6817
      693          1.0498
      812          0.9480
      915          1.0183
     1070          1.1587
     1381          1.2640
     2829          1.7439
     3346          1.8844
     3863          1.9546

Adsorbent       : 3A MSC          Adsorbent       : 3A MSC
Adsorbate       : Methane         Adsorbate       : Methane
Adsorption Temp :  0°C            Adsorption Temp :  0°C
Figure number   : 19             Figure number   : 19
Notes           : 1st run         Notes           : 2nd run

   P (Torr)      q (mmol/g)         P (Torr)      q (mmol/g)
        8          0.2330              4           0.1039
       47          0.3051             87           0.3006
      108          0.4683            167           0.4583
      229          0.6589            308           0.6434
      375          0.8048            643           0.8919
      628          0.9599           1204           1.5612
      917          1.1160           2133           1.9740
     1216          1.3370           3146           2.2850
     1428          1.5234           3938           2.4997
     1753          1.8290
     2086          2.0056
     2505          2.1520
     2963          2.2283
     3603          2.4385
     4122          2.5680
```

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Adsorbent	: 3A MSC
Adsorbate	: Methane
Adsorption Temp	: 30°C
Figure number	: 19
Notes	: 1st run

P (Torr)	q (mmol/g)
812	1.4083
915	1.4783
1070	1.5663
1380	1.7592
1794	1.9547
2311	2.0856
2828	2.1660
3345	2.2716

Adsorbent	: 3A MSC
Adsorbate	: Methane
Adsorption Temp	: 50°C
Figure number	: 19
Notes	: 1st run

P (Torr)	q (mmol/g)
10	0.3670
25	0.3840
90	0.4020
130	0.4040
210	0.4640
320	0.5420
471	0.6210
648	0.7920
845	0.9310
1070	1.0950
1315	1.2190
1481	1.2480
1710	1.2870
2040	1.3790
3270	1.5770

Adsorbent	: 3A MSC
Adsorbate	: Methane
Adsorption Temp	: 30°C
Figure number	: 19
Notes	: 2nd run

P (Torr)	q (mmol/g)
18	0.2340
28	0.2510
82	0.3191
123	0.3618
161	0.5964
220	0.6646
280	0.7329
360	0.9268
430	1.0370
525	1.1812
634	1.3258
745	1.4371
877	1.5655
985	1.6934
1250	1.8086
1675	1.9111
1930	2.0010
2493	2.0820

Adsorbent	: 3A MSC
Adsorbate	: Methane
Adsorption Temp	: 50°C
Figure number	: 19
Notes	: 2nd run

P (Torr)	q (mmol/g)
44	0.4106
530	0.7740
590	0.8090
690	0.8700
867	0.9998
1045	1.0879
1340	1.1957
1610	1.2778
2470	1.5336

```
Adsorbent          : 5A MSC          Adsorbent          : 5A MSC
Adsorbate          : Nitrogen        Adsorbate          : Nitrogen
Adsorption Temp  :  0°C              Adsorption Temp  :  0°C
Figure number    : 21               Figure number    : 21
Notes            : 1st run          Notes            : 2nd run

    P (Torr)      q (mmol/g)           P (Torr)      q (mmol/g)
        23         0.1424                  11          0.1422
        79         0.2122                 110          0.2587
       143         0.2797                 193          0.3368
       230         0.3629                 314          0.4438
       357         0.4649                 480          0.5570
       508         0.5726                 629          0.6520
       665         0.6703                 810          0.7402
       924         0.7933                1097          0.8742
      1162         0.8880                1384          0.9727
      1445         0.9914                1740          1.0932
      1791         1.0989                2142          1.1845
      2204         1.2133                2453          1.2886
      2624         1.3201                3006          1.4167
      3125         1.4190                3475          1.5021
      3631         1.5179                4087          1.6063
      4232         1.6268                4724          1.6908
                                         5617          1.7870


Adsorbent          : 5A MSC          Adsorbent          : 5A MSC
Adsorbate          : Nitrogen        Adsorbate          : Nitrogen
Adsorption Temp  : 30°C              Adsorption Temp  : 50°C
Figure number    : 21               Figure number    : 21
Notes            :                  Notes            : 1st run

    P (Torr)      q (mmol/g)           P (Torr)      q (mmol/g)
        23         0.0916                 750          0.4233
       108         0.1317                1034          0.4985
       227         0.1853                1427          0.5501
       418         0.2584                1858          0.6290
       693         0.3589                2288          0.6852
      1007         0.4554                2762          0.7577
      1337         0.5522                3493          0.8594
      1696         0.6549                4181          0.9486
      2129         0.7847                5623          1.1287
      2483         0.8619
      2995         0.9862
      3543         1.1164
      4112         1.1814
      4526         1.2399
      5330         1.3387
      6100         1.3936
```

```
Adsorbent        : 5A MSC              Adsorbent        : 3A MSC
Adsorbate        : Nitrogen            Adsorbate        : Nitrogen
Adsorption Temp  : 50°C                Adsorption Temp  : 0°C
Figure number    : 21                  Figure number    : 22
Notes            : 2nd run             Notes            : 1st run

   P (Torr)      q (mmol/g)              P (Torr)      q (mmol/g)
      24           0.0790                   10           0.1042
      71           0.1156                   73           0.1800
     163           0.1634                  153           0.2748
     337           0.2083                  305           0.4308
     594           0.2932                  485           0.5727
    1055           0.4137                  667           0.6663
    1438           0.4790                  907           0.7689
    2061           0.6187                 1334           0.8873
    2791           0.7434                 1823           1.0185
    3972           0.9099                 2438           1.1565
    5915           1.1337                 3039           1.2423
                                          4025           1.3638
Adsorbent        : 3A MSC               5392           1.5060
Adsorbate        : Nitrogen            7021           1.6661
Adsorption Temp  : 0°C
Figure number    : 22                  Adsorbent        : 3A MSC
Notes            : 2nd run             Adsorbate        : Nitrogen
                                       Adsorption Temp  : 30°C
   P (Torr)      q (mmol/g)            Figure number    : 22
      16           0.1376              Notes            : 2nd run
      64           0.1982
     120           0.2701                 P (Torr)      q (mmol/g)
     243           0.3956                   290           0.3364
     406           0.5184                   580           0.4487
     632           0.6651                  1000           0.5786
     919           0.8096                  1700           0.7538
    1355           0.9802                  2500           0.9076
    2087           1.1545                  3500           1.0665
    3113           1.3400                  4500           1.1729
    4595           1.5000                  5470           1.2834
    6826           1.6641                  6490           1.3569
                                           7580           1.4275
Adsorbent        : 3A MSC
Adsorbate        : Nitrogen
Adsorption Temp  : 30°C
Figure number    : 22
Notes            : 1st run

   P (Torr)      q (mmol/g)
     812           0.3975
     915           0.4871
    1019           0.4994
    1432           0.6259
    1536           0.6382
    1872           0.6950
```

```
Adsorbent      : 3A MSC          Adsorbent      : 3A MSC
Adsorbate      : Nitrogen        Adsorbate      : Nitrogen
Adsorption Temp : 50°C           Adsorption Temp : 50°C
Figure number  : 22              Figure number  : 22
Notes          :                 Notes          :

  P (Torr)    q (mmol/g)           P (Torr)    q (mmol/g)
     85         0.1674                139         0.2264
    200         0.2110                252         0.2590
    425         0.2776                406         0.3037
    735         0.3492                614         0.3647
   1065         0.4417                942         0.4362
   1545         0.5611               1456         0.5495
   1990         0.6652               2215         0.6987
   2450         0.7378               2881         0.8011
   2910         0.8335               3854         0.9557
   3440         0.9079               4981         1.0437
   3895         0.9716
   5000         1.0779
   5630         1.1287
   6030         1.1794

Adsorbent      : 5A MSC          Adsorbent      : 5A MSC
Adsorbate      : Argon           Adsorbate      : Argon
Adsorption Temp : 0°C            Adsorption Temp : 0°C
Figure number  : 23              Figure number  : 23
Notes          : 1st run         Notes          : 2nd run

  P (Torr)    q (mmol/g)           P (Torr)    q (mmol/g)
    142         0.1754                145         0.1913
    225         0.2465                233         0.2626
    321         0.3233                360         0.3667
    456         0.4206                459         0.4400
    553         0.4850                560         0.5063
    684         0.5627                775         0.6285
    810         0.6385               1210         0.8378
    970         0.7170               1714         1.0347
   1168         0.8052               2586         1.3081
   1342         0.8858               3661         1.5619
   1496         0.9410               4857         1.7533
   1637         0.9960               6012         1.9118
   2071         1.1398               7198         2.0286
   2514         1.2714
   2994         1.4022
   3506         1.5126
   4004         1.6014
   5005         1.7631
   5935         1.8858
   7145         2.0015
```

Adsorbent	: 5A MSC
Adsorbate	: Argon
Adsorption Temp	: 30°C
Figure number	: 23
Notes	: 1st run

P (Torr)	q (mmol/g)
13	0.1191
36	0.1381
103	0.1847
174	0.2102
312	0.2691
530	0.3591
810	0.4401
1167	0.5890
1273	0.6286
2016	0.8189
2147	0.8539
2885	0.9254
3200	0.9809
4150	1.0894
4397	1.1326
5736	1.2879
6957	1.4218

Adsorbent	: 5A MSC
Adsorbate	: Argon
Adsorption Temp	: 30°C
Figure number	: 23
Notes	: 2nd run

P (Torr)	q (mmol/g)
22	0.0928
77	0.1172
175	0.1676
315	0.2350
530	0.3184
782	0.4100
1010	0.5079
1530	0.6382
2025	0.7624
2505	0.8757
3157	1.0057
3570	1.0765

Adsorbent	: 5A MSC
Adsorbate	: Argon
Adsorption Temp	: 50°C
Figure number	: 23
Notes	:

P (Torr)	q (mmol/g)
980	0.3194
1533	0.4488
2035	0.5308
2545	0.6218
3178	0.7319
3633	0.8038
4167	0.8918
5145	1.0213
6100	1.1165
7420	1.2636
8147	1.3264
9520	1.4339

Adsorbent	: 5A MSC
Adsorbate	: Argon
Adsorption Temp	: 50°C
Figure number	: 23
Notes	:

P (Torr)	q (mmol/g)
31	0.0309
105	0.0505
236	0.0892
407	0.1325
610	0.1855
895	0.2583
1225	0.3357
1689	0.4467
2168	0.5403
3045	0.6901
4296	0.8794
5260	1.0066
6429	1.1319
7973	1.2720
9974	1.4804

Adsorbent	: 3A MSC
Adsorbate	: Argon
Adsorption Temp	: 0°C
Figure number	: 24
Notes	: 1st run

P (Torr)	q (mmol/g)
227	0.2936
368	0.3750
614	0.5498
877	0.6861
1288	0.8392
1656	0.9886
2111	1.1738
2762	1.2967
3537	1.4227
6167	1.7824

Adsorbent	: 3A MSC
Adsorbate	: Argon
Adsorption Temp	: 30°C
Figure number	: 24
Notes	:

P (Torr)	q (mmol/g)
50	0.2390
100	0.2600
200	0.3100
350	0.3670
550	0.4460
800	0.5330
1150	0.6250
1800	0.7890
2240	0.8740
3040	1.0150
4300	1.1980
5980	1.3610
8030	1.5110
9960	1.6470

Adsorbent	: 3A MSC
Adsorbate	: Argon
Adsorption Temp	: 0°C
Figure number	: 24
Notes	: 2nd run

P (Torr)	q (mmol/g)
40	0.1463
146	0.2553
365	0.4139
616	0.5318
867	0.6523
1196	0.7903
1512	0.9203
2029	1.1097
2292	1.1761
2737	1.2963
3269	1.3902
3717	1.5053
4312	1.5878
4969	1.6693
5647	1.7669
6322	1.8307

Adsorbent	: 3A MSC
Adsorbate	: Argon
Adsorption Temp	: 30°C
Figure number	: 24
Notes	:

P (Torr)	q (mmol/g)
400	0.3388
770	0.4555
1210	0.5774
1870	0.7383
2980	0.9945
4290	1.1619
5750	1.3599
8180	1.5590
9980	1.6147

Adsorbent	: 3A MSC		Adsorbent	: 3A MSC
Adsorbate	: Argon		Adsorbate	: Argon
Adsorption Temp	: 50°C		Adsorption Temp	: 50°C
Figure number	: 24		Figure number	: 24
Notes	:		Notes	:

P (Torr)	q (mmol/g)		P (Torr)	q (mmol/g)
58	0.1352		9	0.0496
90	0.1786		79	0.1085
170	0.1988		240	0.1593
290	0.2302		535	0.2395
500	0.2822		858	0.3178
820	0.3673		1461	0.4525
1155	0.4305		2130	0.5915
1560	0.5157		2935	0.7054
1985	0.5772		4776	0.9234
2420	0.6490		6710	1.1308
2780	0.7169			
3060	0.7625			
3520	0.8288			
3950	0.8721			
4560	0.9606			
4980	0.9975			
6010	1.0622			

Adsorbent	: 5A MSC		Adsorbent	: 5A MSC
Adsorbate	: Oxygen		Adsorbate	: Oxygen
Adsorption Temp	: 30°C		Adsorption Temp	: 30°C
Figure number	: 25		Figure number	: 25
Notes	: 1st run		Notes	: 2nd run

P (torr)	q (mmol/g)		P (torr)	q (mmol/g)
0.0	0.0000		0.0	0.0000
13.2	0.0051		12.2	0.0037
49.4	0.0253		49.8	0.0231
106.9	0.0532		87.7	0.0422
132.7	0.0653		214.6	0.1068
187.4	0.0903		361.0	0.1674
269.4	0.1274		510.3	0.2294
365.8	0.1693		539.8	0.2419
388.6	0.1792		666.3	0.2944
476.0	0.2162		596.4	0.2662
636.0	0.2863		663.1	0.2966
706.2	0.3212			

```
Adsorbent        : 5A MSC
Adsorbate        : Nitrogen
Adsorption Temp  : 30°C
Figure number    : 25
Notes            : 1st. run
```

P (torr)	q (mmol/g)
0.2	0.0940
1.8	1.4410
3.9	3.1260
8.1	5.9930
12.6	8.6210

```
Adsorbent        : 5A MSC
Adsorbate        : Nitrogen
Adsorption Temp  : 30°C
Figure number    : 25
Notes            : 2nd. run
```

P (torr)	q (mmol/g)
23.4	0.0138
77.5	0.0448
172.8	0.0954
274.7	0.1466
299.3	0.1590
451.1	0.2268
610.1	0.2930

```
Adsorbent        : 3A MSC
Adsorbate        : Methane
Adsorption Temp  : 30°C
Figure number    : 26
Notes            :
```

P (Torr)	q (mmol/g)
812	1.4083
915	1.4783
1070	1.5663
1380	1.7592
1794	1.9547
2311	2.0856
2828	2.1660
3345	2.2716

```
Adsorbent        : 3A MSC
Adsorbate        : Methane
Adsorption Temp  : 30°C
Figure number    : 26
Notes            :
```

P (Torr)	q (mmol/g)
18	0.2340
28	0.2510
82	0.3191
123	0.3618
161	0.5964
220	0.6646
280	0.7329
360	0.9268
430	1.0370
525	1.1812
634	1.3258
745	1.4371
877	1.5655
985	1.6934
1250	1.8086
1675	1.9111
1930	2.0010
2493	2.0820

```
Adsorbent        : 5A MSC
Adsorbate        : Methane
Adsorption Temp  : 30°C
Figure number    : 26
Notes            :
```

P (Torr)	q (mmol/g)
812	0.9686
915	1.0415
1070	1.1858
1380	1.2990
1794	1.5085
2311	1.6855
2828	1.8156
3345	1.9692
3862	2.0525

```
Adsorbent        : B-F MSC              Adsorbent        : 5A MSC
Adsorbate        : Methane             Adsorbate        : Methane
Adsorption Temp  : 30°C                Adsorption Temp  : 30°C
Figure number    : 26                  Figure number    : 26
Notes            :                     Notes            :
   P (Torr)      q (mmol/g)              P (Torr)       q (mmol/g)
        18        0.0184                      25         0.1325
       273        0.4311                      60         0.2520
       521        0.6007                     125         0.2800
       732        0.7297                     230         0.4871
       981        0.8734                     305         0.5549
      1427        1.0781                     472         0.7041
      2037        1.1609                     712         0.8684
      3239        1.3341                     970         1.0398
      4220        1.4262                    1186         1.1705
      5221        1.4815                    1500         1.3037
                                            1874         1.4582
Adsorbent        : 3A MSC                    1980         1.4939
Adsorbate        : Oxygen                    2383         1.6557
Adsorption Temp  : 30°C                      2682         1.7358
Figure number    : 27                        2928         1.8014
Notes            : 1st run                   3402         1.9123
                                             3922         2.0441
   P (Torr)      q (mmol/g)         Adsorbent        : 3A MSC
       812        0.3856            Adsorbate        : Oxygen
       915        0.4301            Adsorption Temp  : 30°C
      1019        0.4579            Figure number    : 27
      1432        0.5859            Notes            : 2nd run
      1536        0.6137              P (Torr)       q (mmol/g)
      2053        0.7610                     17         0.0798
      2518        0.8483                     25         0.0842
      3087        0.9676                     66         0.0936
      3190        0.9828                    130         0.1202
      3862        1.0964                    186         0.1467
                                            252         0.1818
Adsorbent        : 5A MSC                    332         0.2089
Adsorbate        : Oxygen                    432         0.2448
Adsorption Temp  : 30°C                      577         0.3070
Figure number    : 27                        756         0.3867
Notes            : 1st run                   967         0.4714
                                            1197         0.5274
   P (Torr)      q (mmol/g)                 1424         0.5958
       812        0.2934                    1797         0.6971
       915        0.3316                    2213         0.7954
      1070        0.3711                    2575         0.8714
      1277        0.4653                    2893         0.9337
      1525        0.5250                    3220         0.9921
      1949        0.6662                    3536         1.0503
      2352        0.7654                    3973         1.1031
      2818        0.8662                    4513         1.1836
      3345        0.9982                    5046         1.2473
      3862        1.1062                    5590         1.3112
                                            6164         1.3750
                                            6591         1.4200
```

```
Adsorbent        : 5A MSC
Adsorbate        : Oxygen
Adsorption Temp  : 30°C
Figure number    : 27
Notes            : 2nd run

    P (Torr)        q (mmol/g)
       812            0.3308
       915            0.3685
      1081            0.4430
      1380            0.5442
      1794            0.6484
      2311            0.7844
      2828            0.9028
      3345            0.9979
      3862            1.0929


Adsorbent        : 5A MSC
Adsorbate        : Oxygen
Adsorption Temp  : 30°C
Figure number    : 27
Notes            : 4nd run
    P (Torr)        q (mmol/g)
        13           0.0055
        49           0.0255
       107           0.0534
       133           0.0654
       187           0.0903
       269           0.1272
       366           0.1693
       389           0.1791
       476           0.2162
       596           0.2662
       636           0.2863
```

```
Adsorbent        : 5A MSC
Adsorbate        : Oxygen
Adsorption Temp  : 30°C
Figure number    : 27
Notes            : 3nd run

    P (Torr)        q (mmol/g)
       812            0.3483
       915            0.3860
      1019            0.4296
      1432            0.5630
      1536            0.5949
      2053            0.7426
      2570            0.8552
      2673            0.8812
      3216            1.0003
      3345            1.0153
      3862            1.0986


Adsorbent        : 5A MSC
Adsorbate        : Oxygen
Adsorption Temp  : 30°C
Figure number    : 27
Notes            : 5nd run
    P (Torr)        q (mmol/g)
        12           0.0040
        50           0.0233
        88           0.0422
       215           0.1067
       361           0.1672
       510           0.2293
       540           0.2418
       666           0.2942


Adsorbent        : B-F MSC
Adscrbate        : Oxygen
Adsorption Temp  : 30°C
Figure number    : 27
Notes            :
    P (Torr)        q (mmol/g)
         8           0.1100
        72           0.1520
       178           0.1890
       344           0.2390
       645           0.3220
      1097           0.4360
      1553           0.5800
      2116           0.6850
      2748           0.7510
      3108           0.8220
      3643           0.9060
      4298           0.9880
      4505           1.0160
```

Adsorbent	: 3A MSC
Adsorbate	: Nitrogen
Adsorption Temp	: 30°C
Figure number	: 28
Notes	:

P (Torr)	q (mmol/g)
35	0.2203
130	0.2609
290	0.3364
580	0.4487
1000	0.5786
1700	0.7538
2500	0.9076
3500	1.0665
4500	1.1729
5470	1.2834
6490	1.3569
7580	1.4275
9870	1.5285

Adsorbent	: 5A MSC
Adsorbate	: Nitrogen
Adsorption Temp	: 30°C
Figure number	: 28
Notes	:

P (Torr)	q (mmol/g)
23	0.0916
108	0.1317
227	0.1853
418	0.2584
693	0.3589
1007	0.4554
1337	0.5522
1696	0.6549
2129	0.7847
2483	0.8619
2995	0.9862
3543	1.1164
4112	1.1814
4526	1.2399
5330	1.3387
6100	1.3936

Adsorbent	: B-F MSC
Adsorbate	: Nitrogen
Adsorption Temp	: 30°C
Figure number	: 28
Notes	:

P (Torr)	q (mmol/g)
8	0.1230
67	0.1500
181	0.1900
397	0.2440
721	0.2560
1160	0.3520
1951	0.5070
2717	0.6290
3558	0.7190
4243	0.8110
5113	0.8760
5492	0.8910
6892	0.9840
8419	1.0720
9468	1.1300

Adsorbent	: 3A MSC
Adsorbate	: Argon
Adsorption Temp	: 30°C
Figure number	: 29
Notes	: 1st run

P (Torr)	q (mmol/g)
50	0.2390
100	0.2600
200	0.3100
350	0.3670
550	0.4460
800	0.5330
1150	0.6250
1800	0.7890
2240	0.8740
3040	1.0150
4300	1.1980
5980	1.3610
8030	1.5110
9960	1.6470

Adsorbent	: 5A MSC
Adsorbate	: Argon
Adsorption Temp	: 30°C
Figure number	: 29
Notes	: 1st run

P (Torr)	q (mmol/g)
13	0.1191
36	0.1381
103	0.1847
174	0.2102
312	0.2691
530	0.3591
810	0.4401
1167	0.5890
1273	0.6286
2016	0.8189
2147	0.8539
2885	0.9254
3200	0.9809
4150	1.0894
4397	1.1326
5736	1.2879
6957	1.4218

Adsorbent	: 3A MSC
Adsorbate	: Argon
Adsorption Temp	: 30°C
Figure number	: 29
Notes	: 2nd run

P (Torr)	q (mmol/g)
400	0.3388
770	0.4555
1210	0.5774
1870	0.7383
2980	0.9945
4290	1.1619
5750	1.3599
8180	1.5590
9980	1.6147

Adsorbent	: B-F MSC
Adsorbate	: Argon
Adsorption Temp	: 30°C
Figure number	: 29
Notes	:

P (Torr)	q (mmol/g)
18	0.0646
63	0.0818
135	0.0996
278	0.1614
515	0.2195
965	0.3251
1421	0.4550
1828	0.5334
2729	0.6966
3019	0.7300
4079	0.7970
4321	0.8211
4525	0.8484
6604	1.0213
6817	1.0428
8519	1.1561
9654	1.2309

Adsorbent	: 5A MSC
Adsorbate	: Argon
Adsorption Temp	: 30°C
Figure number	: 29
Notes	: 3nd run

P (Torr)	q (mmol/g)
22	0.0928
77	0.1172
175	0.1676
315	0.2350
530	0.3184
782	0.4100
1010	0.5079
1530	0.6382
2025	0.7624
2505	0.8757
3157	1.0057
3570	1.0765

Adsorbent	: 3A MSC		Adsorbent	: 3A MSC
Adsorbate	: Nitrogen		Adsorbate	: Argon
Adsorption Temp	: 0°C		Adsorption Temp	: 0°C
Figure number	: 33		Figure number	: 33
Notes	: 153 Torr		Notes	: 227 Torr

Time (sec)	Mt/M_∞	Time (sec)	Mt/M_∞
1	0.0004	2	0.0593
2	0.0151	4	0.0663
3	0.0230	6	0.0671
4	0.0276	10	0.1445
5	0.0351	20	0.1607
6	0.0362	30	0.1832
8	0.0399	50	0.3190
10	0.0435	100	0.4144
10	0.0450	140	0.4600
14	0.0519	160	0.4900
16	0.0619	180	0.5200
18	0.0667	200	0.5600
20	0.0772	300	0.6000
25	0.0860	400	0.6542
30	0.0926	500	0.6900
35	0.1010	600	0.7300
40	0.1108	700	0.7600
45	0.1224	800	0.8000
50	0.1332	900	0.8300
60	0.1792	1000	0.8500
30	0.2186	1100	0.8700
100	0.2564	1200	0.8900
150	0.2920	1300	0.9200
200	0.3263	1400	0.9400
250	0.3552	1500	0.9500
300	0.3840	1600	0.9600
350	0.4120	1700	0.9700
400	0.4332	1800	0.9780
450	0.4597		
550	0.5039		
700	0.5446		
850	0.5789		
1000	0.6147		
1150	0.6457		
1300	0.6823		
1450	0.7080		
1600	0.7421		
1800	0.7632		
2000	0.7858		
2200	0.8120		
2400	0.8287		
2600	0.8536		
2800	0.8699		
3000	0.8887		

Adsorbent	: 3A MSC		Adsorbent	: 3A MSC
Adsorbate	: Oxygen		Adsorbate	: Methane
Adsorption Temp	: 0°C		Adsorption Temp	: 0°C
Figure number	: 33		Figure number	: 33
Notes	: 680 Torr		Notes	: 510 Torr

Time (sec)	Mt/M_∞	Time (sec)	Mt/M_∞
2	0.0339	2	0.0218
3	0.0486	52	0.0453
4	0.1101	152	0.1044
5	0.1629	202	0.1549
6	0.2138	352	0.1982
7	0.2463	452	0.2298
8	0.2915	552	0.2526
9	0.3304	652	0.2737
10	0.3612	852	0.3258
12	0.3934	1052	0.3666
14	0.4229	1152	0.3901
16	0.4714	1352	0.4075
18	0.5349	1452	0.4192
20	0.5831	1552	0.4516
25	0.6194	1652	0.4853
30	0.6579	1852	0.5108
35	0.6886	2352	0.5515
40	0.7089	2852	0.5776
45	0.7305		
50	0.7604		
70	0.7938		
270	0.9672		
370	0.9828		
770	0.9982		

Adsorbent	: 3A MSC
Adsorbate	: Argon
Adsorption Temp	: 30°C
Figure number	: 34
Notes	: 400 Torr

Time (sec)	Mt/M_∞	Time (sec)	Mt/M_∞
40	0.2998	400	0.8447
40	0.3877	440	0.8663
60	0.4319	480	0.8848
80	0.4689	520	0.9003
100	0.5059	560	0.9141
120	0.5383	600	0.9388
140	0.5718	680	0.9568
160	0.5985	760	0.9681
180	0.6278	840	0.9784
200	0.6751	920	0.9846
240	0.7188	1000	0.9913
280	0.7573	1080	0.9964
320	0.7887		
360	0.8170		

Adsorbent	: 3A MSC		Adsorbent	: 3A MSC
Adsorbate	: Nitrogen		Adsorbate	: Oxygen
Adsorption Temp	: 30°C		Adsorption Temp	: 30°C
Figure number	: 34		Figure number	: 34
Notes	: 650 Torr		Notes	: 1540 Torr

Time (sec)	Mt/M_∞		Time (sec)	Mt/M_∞
24	0.0006		15	0.0058
70	0.4575		10	0.6012
80	0.4822		20	0.8585
100	0.5019		30	0.9061
120	0.5217		40	0.9307
160	0.5759		50	0.9465
200	0.6252		60	0.9578
240	0.6548		70	0.9654
280	0.6992		80	0.9722
320	0.7337		90	0.9794
360	0.7534		100	0.9870
600	0.8767		120	1.0000
840	0.9310		140	1.0000
			160	1.0000
			180	1.0000
			200	1.0000

Adsorbent	: 3A MSC
Adsorbate	: Methane
Adsorption Temp	: 30°C
Figure number	: 34
Notes	: 815 Torr

Time (sec)	Mt/M_∞	Time (sec)	Mt/M_∞
5	0.0000	240	0.2700
10	0.0117	260	0.2800
20	0.0273	280	0.2900
30	0.0468	300	0.3000
40	0.0640	350	0.3200
50	0.0824	400	0.3400
60	0.0976	450	0.3600
70	0.1259	500	0.3800
80	0.1539	600	0.4000
90	0.1790	700	0.4200
100	0.2038	800	0.4500
120	0.2100	1000	0.4700
140	0.2200	1200	0.5200
160	0.2300	1400	0.5500
180	0.2400	1600	0.5800
200	0.250	2000	0.6100
220	0.2600		

Adsorbent	: 3A MSC		Adsorbent	: 3A MSC
Adsorbate	: Nitrogen		Adsorbate	: Argon
Adsorption Temp	: 50°C		Adsorption Temp	: 50°C
Figure number	: 35		Figure number	: 35
Notes	: 200 Torr		Notes	: 1461 Torr

Time (sec)	M_t/M_∞	Time (sec)	M_t/M_∞
2	0.0901	2	0.0899
3	0.1636	4	0.1072
5	0.1994	6	0.1339
7	0.2209	8	0.1611
10	0.2533	13	0.2161
13	0.2762	18	0.2566
17	0.2986	23	0.2859
20	0.3301	28	0.3137
23	0.3568	33	0.3502
27	0.3778	43	0.4124
30	0.4074	53	0.4636
33	0.4365	63	0.5000
37	0.4580	73	0.5373
44	0.4857	83	0.5680
51	0.5210	93	0.5959
57	0.5243	103	0.6196
64	0.5539	113	0.6390
71	0.5935	123	0.6605
77	0.6064	133	0.6723
84	0.6355	183	0.7436
91	0.6631	233	0.7987
97	0.6903	283	0.8473
104	0.7118	333	0.8897
111	0.7180	383	0.9210
127	0.7500	433	0.9442
144	0.7800	483	0.9631
161	0.8000	533	0.9772
177	0.8250	583	0.9902
194	0.8500	633	0.9981
244	0.8800	733	1.0000
261	0.9000		
277	0.9200		
311	0.9400		
411	0.9600		

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Adsorbent	: 3A MSC		Adsorbent	: 3A MSC
Adsorbate	: Oxygen		Adsorbate	: Methane
Adsorption Temp	: 50°C		Adsorption Temp	: 50°C
Figure number	: 35		Figure number	: 35
Notes	: 725 Torr		Notes	: 962 Torr

Time (sec)	M_t/M_∞		Time (sec)	M_t/M_∞
1	0.1783		10	0.0441
2	0.3545		20	0.1360
3	0.4817		30	0.2278
4	0.5939		40	0.2577
5	0.6822		50	0.2638
7	0.7592		60	0.2756
10	0.8561		70	0.2883
14	0.9388		80	0.2997
18	0.9666		130	0.3510
22	0.9736		200	0.4031
26	0.9869		230	0.4249
35	0.9901		260	0.4485
50	0.9957		290	0.4789
70	0.9983		350	0.5133
90	1.0000		400	0.5460
120	1.0000		500	0.5772
150	1.0000		600	0.6013
200	1.0000		700	0.6305
			800	0.6530
			900	0.6747
			1000	0.6960
			1200	0.7174
			1400	0.7509
			1600	0.7821
			1800	0.8109
			2000	0.8378
			2200	0.8658
			2400	0.8895
			2600	0.9053
			2800	0.9218

Adsorbent	: 3A MSC		Adsorbent	: 3A MSC
Adsorbate	: Argon		Adsorbate	: Argon
Adsorption Temp	: 0°C		Adsorption Temp	: 50°C
Figure number	: 36		Figure number	: 36
Notes	: 227 Torr		Notes	: 1461 Torr

Time (sec)	M_t/M_∞	Time (sec)	M_t/M_∞
2	0.0593	2	0.0899
4	0.0663	4	0.1072
6	0.0671	6	0.1339
10	0.1445	8	0.1611
20	0.1607	13	0.2161
30	0.1832	18	0.2566
50	0.3190	23	0.2859
100	0.4144	28	0.3137
140	0.4600	33	0.3502
160	0.4900	43	0.4124
180	0.5200	53	0.4636
200	0.5600	63	0.5000
300	0.6000	73	0.5373
400	0.6542	83	0.5680
500	0.6900	93	0.5959
600	0.7300	103	0.6196
700	0.7600	113	0.6390
800	0.8000	123	0.6605
900	0.8300	133	0.6723
1000	0.8500	183	0.7436
1100	0.8700	233	0.7987
1200	0.8900	283	0.8473
1300	0.9200	333	0.8897
1400	0.9400	383	0.9210
1500	0.9500	433	0.9442
1600	0.9600	483	0.9631
1700	0.9700	533	0.9772
1800	0.9780	583	0.9902
		633	0.9981
		733	1.0000

Adsorbent	: 3A MSC
Adsorbate	: Argon
Adsorption Temp	: 30°C
Figure number	: 36
Notes	: 350 Torr

Time (sec)	M_t/M_∞	Time (sec)	M_t/M_∞
16	0.0004	140	0.6073
30	0.2988	160	0.6413
40	0.3343	200	0.7048
50	0.3652	240	0.7564
60	0.4051	300	0.8125
70	0.4346	370	0.8598
80	0.4656	490	0.9011
100	0.5217	610	0.9365
120	0.5660		

Adsorbent   : 5A MSC
Adsorbate   : Oxygen
Adsorption Temp   : 0°C
Figure number   : none
Notes   : 602 Torr

Time (sec)	Mt/M_∞
3	0.1021
4	0.1710
5	0.1916
8	0.2229
9	0.2856
10	0.3196
11	0.3268
12	0.3384
13	0.3456
14	0.3483
15	0.3778
20	0.4924
25	0.5067
30	0.5389
35	0.5739
40	0.6276
50	0.6759
60	0.7466
70	0.7834
80	0.8241
90	0.8554
120	0.9155
340	0.9973
440	0.9973
490	0.9982
590	1.0000

Diffusivity $(D/r^2) \approx 0.0012$ s^{-1}

Adsorbent   : 5A MSC
Adsorbate   : Oxygen
Adsorption Temp   : 0°C
Figure number   : none
Notes   : 1066 Torr

Time (sec)	Mt/M_∞
2	0.1091
3	0.2329
4	0.2654
5	0.2842
6	0.2973
7	0.3116
8	0.3219
9	0.3316
10	0.3441
11	0.3578
12	0.3721
13	0.3840
14	0.4000
15	0.4125
20	0.4719
25	0.5084
30	0.5705
35	0.5825
40	0.6179
50	0.6812
60	0.7405
70	0.7781
80	0.8124
90	0.8272
100	0.8409
110	0.8688
120	0.9036
130	0.9281
190	0.9470
240	0.9652
290	0.9721
590	0.9772
640	0.9937
740	0.9954
1040	1.0000

Diffusivity $(D/r^2) = 0.0014$ s^{-1}

Adsorbent	: 5A MSC
Adsorbate	: Oxygen
Adsorption Temp	: 0°C
Figure number	: none
Notes	: 2509 Torr

Time (sec)	Mt/M_∞
2	0.1285
3	0.2318
4	0.2626
5	0.2789
6	0.3003
7	0.3160
8	0.3270
9	0.3294
10	0.3508
11	0.3764
12	0.3950
13	0.4124
14	0.4199
15	0.4287
20	0.4867
25	0.5622
30	0.5825
35	0.6243
40	0.6481
50	0.7062
60	0.7654
70	0.7886
80	0.8026
90	0.8531
100	0.8653
110	0.9036
120	0.9065
190	0.9065
240	0.9501
290	0.9512
340	0.9628
390	0.9704
440	0.9750
490	0.9779
590	0.9866
640	0.9977
740	1.0000

Diffusivity $(D/r^2) = 0.0015$ s^{-1}

Adsorbent	: 5A MSC
Adsorbate	: Oxygen
Adsorption Temp	: 0°C
Figure number	: none
Notes	: 3019 Torr

Time (sec)	Mt/M_∞
1	0.0815
2	0.1786
5	0.1801
6	0.1831
7	0.2072
8	0.2343
9	0.2607
10	0.2938
11	0.3239
12	0.3555
13	0.3683
15	0.3811
20	0.4368
25	0.5144
30	0.5626
35	0.5701
40	0.5957
50	0.6875
60	0.7003
70	0.7613
80	0.7809
90	0.8065
110	0.8509
140	0.8785
190	0.9302
340	0.9532
390	0.9613
440	0.9735
640	0.9788
740	0.9824
940	1.0000

Diffusivity $(D/r^2) = 0.0012$ s^{-1}

Adsorbent	: 5A MSC
Adsorbate	: Oxygen
Adsorption Temp	: 50°C
Notes	: 203 Torr

Time (sec)	Mt/M_∞
15	0.3674
55	0.8125
60	0.8131
65	0.8155
75	0.8186
95	0.8204
105	0.8289
115	0.8295
125	0.8379
135	0.8458
145	0.8579
155	0.8627
215	0.9002
265	0.9196
315	0.9565
365	0.9728
415	0.9825
465	0.9958
615	1.0000

Diffusivity $(D/r^2) = 0.014$ s^{-1}

Adsorbent	: 5A MSC
Adsorbate	: Oxygen
Adsorption Temp	: 50°C
Notes	: 920 Torr

Time (sec)	Mt/M_∞
2	0.2866
3	0.4649
4	0.6164
5	0.7175
6	0.7926
7	0.8470
8	0.8858
9	0.9135
10	0.9347
11	0.9478
13	0.9627
15	0.9692
17	0.9726
19	0.9740
76	0.9778
86	0.9858
96	0.9965
116	0.9975
126	0.9993
146	1.0000

Diffusivity $(D/r^2) = 0.016$ s^{-1}

Adsorbent	: 5A MSC
Adsorbate	: Oxygen
Adsorption Temp	: 50°C
Notes	: 347 Torr

Time (sec)	Mt/M_∞
2	0.0186
3	0.3115
4	0.5123
5	0.6497
6	0.7483
8	0.8660
10	0.9200
12	0.9258
14	0.9444
16	0.9506
21	0.9593
36	0.9652
131	0.9668
141	0.9700
191	0.9761
291	0.9803
341	0.9909
441	0.9945
541	0.9967
591	0.3986
641	1.0000

Diffusivity $(D/r^2) = 0.011$ s^{-1}

Adsorbent	: 5A MSC
Adsorbate	: Oxygen
Adsorption Temp	: 50°C
Notes	: 2505 Torr

Time (sec)	Mt/M_∞
2	0.2593
3	0.4664
5	0.6869
7	0.7917
9	0.8395
11	0.8595
13	0.8655
18	0.8704
23	0.8837
28	0.8837
118	0.9667
128	0.9724
138	0.9734
188	0.9789
238	0.9830
288	0.9903
338	0.9958
488	0.9964

Diffusivity $(D/r^2) = 0.011$ s^{-1}

APPENDIX B

(Computer Program for VSM Calculations)

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C SIMULATION OF ADSORPTION EQUILIBRIA BY VSM
C SEE PAGE 11 FOR EQUATIONS AND REFERENCES
C JIN_QU WANG, DEPT. OF CHEMICAL ENG. WORCESTER POLYTECHNIC
C INSTITUTE, WORCESTER, MA 01609,      1989
C
        PROGRAM AVSM3P
        REAL N1IN,N(50),NC(50),N1IN0,N1INF,NN0,NN,NCC(150)
        DIMENSION F0(50),F1(50),F2(50),DALF1N(50),DALF1B(50),
     *            DALF1A(50),DALF2N(50),DALF2B(50),DALF2A(50),
     *            DALF3N(50),DALF3B(50),DALF3A(50),A(10,10)
        DIMENSION F3(50),P(50),X(4),
     *        BB(50),BB1(50),CC(50),CC1(50),CC2(50),CC3(50),
     *        PC(50),CC4(50),DD(50),DD1(50),DAL1(50),DAL2(50),
     *        DAL3(50),PCC(150)
        COMMON /FOUR/ A
        WRITE (*,300)
300     FORMAT(4X,'INPUT SWITCH NUMBER: IF THE UNIT OF PRESSURE')
        WRITE (*,302)
302     FORMAT(4X,'IS psia, INPUT 1; IF THE UNIT OF PRESSURE')
        WRITE (*,304)
304     FORMAT(4X,'IS torr, INPUT 3')
        READ (*,*) SW
        WRITE (*,1)
  1     FORMAT (6X,'INPUT N1IN0, B10,AV0,M')
        READ (*,*) N1IN0,B10,AV0,M
        OPEN (1,FILE='VSMDATA')
        DO 2 I=1,M
        READ (1,*) P(I),N(I)
  2     CONTINUE
        CLOSE (1)
        WRITE (*,310)
310     FORMAT (6X,'INPUT THE MOLECULAR WEIGHT')
        READ (*,*) WM
        WRITE (*,3)
  3     FORMAT (6X,'N1IN0',10X,'B10',10X,'AV0',6X,'WM','M')
        WRITE (*,4)N1IN0,B10,AV0,WM,M
  4     FORMAT (1X,4F12.4,I8,/)
        WRITE (*,5)
  5     FORMAT (10X,'P',14X,'N',)
        DO 9 I=1,M
        WRITE (*,8) P(I),N(I)
  8     FORMAT (4X, 2F12.5)
        IF (SW.LT.2) GOTO 9
        P(I)=P(I)/51.71
        N(I)=N(I)*22.4
  9     CONTINUE
        J=1
 10     N1IN=N1IN0
        B1=B10
        ALFA1V=AV0
        AA=N1IN/B1
        SF0=0.0
        SF1=0.0
        SF2=0.0
```

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```
      SF3=0.0
      SDF1N=0.0
      SDF1B=0.0
      SDF1A=0.0
      SDF2N=0.0
      SDF2B=0.0
      SDF2A=0.0
      SDF3N=0.0
      SDF3B=0.0
      SDF3A=0.0
      DO 30 I=1,M
      BB(I)=N1IN-N(I)
      BB1(I)=N(I)/BB(I)
      CC(I)=N1IN+ALFA1V*N(I)
      CC1(I)=ALFA1V**2*N(I)
      CC2(I)=CC1(I)/CC(I)
      CC3(I)=ALFA1V*N(I)
      CC4(I)=2*N1IN+ALFA1V*N(I)
      DD(I)=N1IN*N(I)*ALFA1V
      DD1(I)=DD(I)/CC(I)**2
      F0(I)=P(I)-AA*BB1(I)*EXP(CC2(I))
      F1(I)=F0(I)*(ALFA1V**2*N(I)**2*N1IN*EXP(CC2(I))
     *      /(B1*BB(I)*CC(I)**2)-BB1(I)*EXP(CC2(I))/B1+
     *      N(I)*N1IN*EXP(CC2(I))/B1/(N1IN-N(I))**2)
      SF1=SF1+F1(I)
      F2(I)=F0(I)*N(I)*N1IN*EXP(CC2(I))/B1**2/(N1IN-
     *      N(I))
      SF2=SF2+F2(I)
      F3(I)=-F0(I)*N(I)*N1IN*(2*CC3(I)/CC(I)-CC1(I)*N(I)/
     *      CC(I)**2)*EXP(CC2(I))/(B1*BB(I))
      SF3=SF3+F3(I)
      DALF1N(I)=2*(2*CC3(I)**2*EXP(CC2(I))/(B1*BB(I)*CC(I)**
     *          2)-2*CC3(I)**2*N1IN*EXP(CC2(I))/(B1*BB(I)
     *      **2*CC(I)**2)-2*CC3(I)**2*N1IN*EXP(CC2(I))/(B1*
     *      BB(I)*CC(I)**3)-ALFA1V**4*N(I)**3*N1IN*EXP(CC2(I))/
     *      (B1*BB(I)*CC(I)**4)+2*N(I)*EXP(CC2(I))/(B1*BB(I)**2)
     *      -2*N(I)*N1IN*EXP(CC2(I))/(B1*BB(I)**3))*F0(I)+2*
     *      (CC3(I)**2*N1IN*EXP(CC2(I))/(B1*BB(I)*CC(I)**2)-
     *      N(I)*EXP(CC2(I))/(B1*BB(I))+N(I)*N1IN*EXP(CC2(I))/
     *      (B1*BB(I)**2))**2
      SDF1N=SDF1N+DALF1N(I)
      DALF1B(I)=2*(-CC3(I)**2*N1IN*EXP(CC2(I))/(B1**2*BB(I)
     *          *CC(I)**2)+N(I)*EXP(CC2(I))/(B1**2*BB(I))-
     *      N(I)*N1IN*EXP(CC2(I))/(B1**2*BB(I)**2))*F0(I)+2*
     *      N(I)*N1IN*EXP(CC2(I))*(CC3(I)**2*N1IN*EXP(CC2(I))/
     *      (B1*BB(I)*CC(I)**2)-N(I)*EXP(CC2(I))/(B1*BB(I))+
     *      N(I)*N1IN*EXP(CC2(I))/(B1*BB(I)**2))/(B1**2*
     *      BB(I))
      SDF1B=SDF1B+DALF1B(I)
      DALF1A(I)=2*(CC3(I)**2*N1IN*(2*CC3(I)/CC(I)-CC3(I)**
     *          2/CC(I)**2)*EXP(CC2(I))/(B1*BB(I)*CC(I)**2)
     *      -N(I)*(2*CC3(I)/CC(I)-CC3(I)**2/CC(I)**2)*EXP(CC2(I))/
     *      (B1*BB(I))+N(I)*N1IN*(2*CC3(I)/CC(I)-CC3(I)**2/
     *      CC(I)**2)*EXP(CC2(I))/(B1*BB(I)**2)+2*DD(I)*N(I)*
```

```
     *     EXP(CC2(I))/(B1*BB(I)*CC(I)**2)-2*CC3(I)**2*N(I)*
     *     N1IN*EXP(CC2(I))/(B1*BB(I)*CC(I)**3))*F0(I)-2*
     *     N(I)*N1IN*(2*CC3(I)/CC(I)-CC3(I)**2/CC(I)**2)*EXP(
     *     CC2(I))*(CC3(I)**2*N1IN*EXP(CC2(I))/(B1*BB(I)*
     *     CC(I)**2)-N(I)*EXP(CC2(I))/(B1*BB(I))+N(I)*N1IN*
     *     EXP(CC2(I))/(B1*BB(I)**2))/(B1*BB(I))
           SDF1A=SDF1A+DALF1A(I)
           DALF2N(I)=-2*CC3(I)**2*N1IN*EXP(CC2(I))*F0(I)/(B1**
     *                2*BB(I)*CC(I)**2)+2*N(I)*EXP(CC2(I))*F0(I)/
     *     (B1**2*BB(I))-2*N(I)*N1IN*EXP(CC2(I))*F0(I)/(B1**
     *     2*BB(I)**2)+2*N(I)*N1IN*EXP(CC2(I))*(CC3(I)**2*
     *     N1IN*EXP(CC2(I))/(B1*BB(I)*CC(I)**2)-N(I)*EXP(
     *     CC2(I))/(B1*BB(I))+N(I)*N1IN*EXP(CC2(I))/(B1*
     *     BB(I)**2))/(B1**2*BB(I))
           SDF2N=SDF2N+DALF2N(I)
           DALF2B(I)=2*(N(I)*N1IN)**2*EXP(2*CC2(I))/(B1**4*
     *                BB(I)**2)-4*N(I)*N1IN*EXP(CC2(I))*F0(I)/
     *     (B1**3*BB(I))
           SDF2B=SDF2B+DALF2B(I)
           DALF2A(I)=2*N(I)*N1IN*(2*CC3(I)/CC(I)-CC3(I)**2/CC(I)
     *                **2)*EXP(CC2(I))*F0(I)/(B1**2*BB(I))-2*
     *     (N(I)*N1IN)**2*(2*CC3(I)/CC(I)-CC3(I)**2/CC(I)**2)*
     *     EXP(2*CC2(I))/(B1**3*BB(I)**2)
           SDF2A=SDF2A+DALF2A(I)
           DALF3N(I)=2*CC3(I)**2*N1IN*(2*CC3(I)/CC(I)-CC3(I)**2/
     *                CC(I)**2)*EXP(CC2(I))*F0(I)/(B1*BB(I)*CC(I)
     *     **2)-2*N(I)*(2*CC3(I)/CC(I)-CC3(I)**2/CC(I)**2)*EXP(
     *     CC2(I))*F0(I)/(B1*BB(I))+2*N(I)*N1IN*(2*CC3(I)/
     *     CC(I)-CC3(I)**2/CC(I)**2)*EXP(CC2(I))*F0(I)/
     *     (B1*BB(I)**2)-2*N(I)*N1IN*(2*CC3(I)**2/CC(I)**3-2*
     *     CC3(I)/CC(I)**2)*EXP(CC2(I))*F0(I)/(B1*BB(I))-2*N(I)*
     *     N1IN*(2*CC3(I)/CC(I)-CC3(I)**2/CC(I)**2)*EXP(CC2(I))*
     *     (CC3(I)**2*N1IN*EXP(CC2(I))/(B1*BB(I)*CC(I)**2)-
     *     N(I)*EXP(CC2(I))/(B1*BB(I))+N(I)*N1IN*EXP(CC2(I))/
     *     (B1*BB(I)**2))/(B1*BB(I))
           SDF3N=SDF3N+DALF3N(I)
           DALF3B(I)=2*N(I)*N1IN*(2*CC3(I)/CC(I)-(CC3(I)/CC(I))
     *                **2)*EXP(CC2(I))*F0(I)/(B1**2*BB(I))-2*
     *     (N(I)*N1IN)**2*(2*CC3(I)/CC(I)-(CC3(I)/CC(I))**2)*
     *     EXP(2*CC2(I))/(B1**3*BB(I)**2)
25         SDF3B=SDF3B+DALF3B(I)
           DALF3A(I)=-2*N(I)*N1IN*(2*CC3(I)/CC(I)-(CC3(I)/CC(I))
     *                **2)**2*EXP(CC2(I))*F0(I)/(B1*BB(I))-2*N(I)
     *     *N1IN*(2*N(I)/CC(I)-4*CC3(I)*N(I)/CC(I)**2+2*CC3(I)**
     *     2*N(I)/CC(I)**3)*EXP(CC2(I))*F0(I)/(B1*BB(I))+2*(N(I)
     *     *N1IN)**2*(2*CC3(I)/CC(I)-CC3(I)**2/CC(I)**2)**2*
     *     EXP(2*CC2(I))/(B1*BB(I))**2
           SDF3A=SDF3A+DALF3A(I)
30         CONTINUE
           WRITE (*,40)
40         FORMAT (10X,'I',6X,'J',6X,'SF1',6X,'SF2',6X,'SF3',/)
           WRITE (*,45) I,J,SF1,SF2,SF3
45         FORMAT (2X,2I8,3E12.4)
           A(1,1)=SDF1N
```

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```fortran
          A(1,2)=SDF1B
          A(1,3)=SDF1A
          A(1,4)=-SF1
          A(2,1)=SDF2N
          A(2,2)=SDF2B
          A(2,3)=SDF2A
          A(2,4)=-SF2
          A(3,1)=SDF3N
          A(3,2)=SDF3B
          A(3,3)=SDF3A
          A(3,4)=-SF3
          K=3
          NP1=K+1
          CALL GAUSS (X,K,NP1)
          DALTAN=X(1)
          DALTAB=X(2)
          DALTAA=X(3)
          N1INF=N1IN+DALTAN
          B1F=B1+DALTAB
          ALF1VF=ALFA1V+DALTAA
          WRITE(*,55)
55        FORMAT(/,8X,'DALTAN',10X,'DALTAB',10X,'DALTAA')
          WRITE(*,60) DALTAN,DALTAB,DALTAA
60        FORMAT(1X,3E15.6 )
          WRITE(*,65)
65        FORMAT(/,8X,'N1INF',10X,'B1F',10X,'ALFA1VF' )
          WRITE(*,70) N1INF,B1F,ALF1VF
70        FORMAT(1X,3E15.6)
          IF (ABS(DALTAN).GT.0.000001) GOTO 72
          IF (ABS(DALTAB).GT.0.000001) GOTO 72
          IF (ABS(DALTAA).LT.0.000001) GOTO 80
72        IF (ABS(SF1).GT.0.001 ) GOTO 75
          IF (ABS(SF2).GT.0.001 ) GOTO 75
          IF (ABS(SF3).LT.0.001 ) GOTO 80
75        N1IN0=N1INF
          B10=B1F
          AV0=ALF1VF
          J=J+1
          GOTO 10
80        WRITE(*,85)
85        FORMAT(6X,'J',6X,'N1INF',8X,'B1F',8X,'ALFA1VF')
          WRITE(*,90) J,N1INF,B1F,ALF1VF
90        FORMAT(1X,I8,3F15.4,/)
          SR=0.0
          DO 100 K=1,M
          PC(K)=N(K)*N1INF*EXP(ALF1VF**2*N(K)/(N1INF+ALF1VF*N(K)))/
     *          (B1F*(N1INF-N(K)))
          SR=SR+(P(K)-PC(K))**2
100       CONTINUE
          ER0=SR/M
          ER=(ER0)**(0.5)
          WRITE (*,101) N1INF,B1F,ALF1VF
101       FORMAT (4x,'VSM Parameter: N1INF=',E9.4,3X,'B1F=',E9.4,
     *             3X,'ALF1VF=',E10.4,/)
```

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```fortran
          PAUSE 102
102       WRITE(*,105)
105       FORMAT(6X,'I',8X,'P',14X,'PC',16X,'N',/)
          DO 115 I=1,M
          P(I)=P(I)*51.71
          PC(I)=PC(I)*51.71
          N(I)=N(I)/22.4
          WRITE(*,110) I,P(I),PC(I),N(I)
110       FORMAT(1X,I6,3F15.8)
115       CONTINUE
          WRITE (*,120) ER
120       FORMAT (/,6X,'ER=',F12.6)
125       NCC(1)=0.0
          PCC(1)=0.0
          DAN=(N(M)*22.4+5)/100
          DO 130 I=2,100
          NCC(I)=NCC(I-1)+DAN
          PCC(I)=NCC(I)*N1INF*EXP(ALF1VF**2*NCC(I)/(N1INF+
     *           ALF1VF*NCC(I)))/(B1F*(N1INF-NCC(I)))
130       CONTINUE
          OPEN (2,FILE='VSMC100.DAT')
          DO 150 I=1,100
          PCC(I)=PCC(I)*51.71
          NCC(I)=NCC(I)/22.4
          WRITE (2,*) PCC(I),NCC(I)
150       CONTINUE
          CLOSE (2)
          END
C-----------------------------------------------------------
          SUBROUTINE GAUSS (X,N1,NP1)
          DIMENSION X(10),A(10,10)
          COMMON /FOUR/ A
C         THIS SUBROUTINE SOLVES A SYSTEM OF N LINEAR
          DO 100 K=1,N1
          IF(K.EQ.N1) GOTO 30
          KP1=K+1
          L=K
          DO 10 I=KP1,N1
          IF(ABS(A(I,K)).GT.ABS(A(L,K))) L=I
10        CONTINUE
          IF(L.EQ.K) GOTO 30
          DO 20 J=K,NP1
          C=A(K,J)
          A(K,J)=A(L,J)
          A(L,J)=C
20        CONTINUE
30        PIVOT=A(K,K)
          DO 40 J=K,NP1
          A(K,J)=A(K,J)/PIVOT
40        CONTINUE
          DO 60 I=1,N1
          IF(I.EQ.K) GOTO 60
          FACTOR=A(I,K)
          DO 50 J=K,NP1
```

```fortran
        A(I,J)=A(I,J)-FACTOR*A(K,J)
50      CONTINUE
60      CONTINUE
100     CONTINUE
        DO 200 I=1,N1
        X(I)=A(I,NP1)
200     CONTINUE
        RETURN
        END
```